Ministère de l'Environnement
du Québec

Environnement Canada

Northeast States for Coordinated
Air Use Management

# Actes de la conférence

# Conference proceedings

# Symposium nord-américain sur les oxydants

# North American Oxidant Symposium

Québec,
les 25, 26 et 27 février 1987

Québec,
February, 25, 26 and 27, 1987

SYMPOSIUM NORD-AMÉRICAIN SUR LES OXYDANTS

QUÉBEC, les 25, 26 ET 27 FÉVRIER 1987

NORTH AMERICAN OXIDANT SYMPOSIUM

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Northeast States for Coordinated Air Use Management (NESCAUM)

**Objectifs du Symposium**

Faire le point sur l'état actuel des connaissances relatives à la formation, à la surveillance, au transport et à la modélisation des oxydants à la lumière de leurs répercussions sur la santé humaine et sur les écosystèmes terrestres.

**Objectives of the Symposium**

Presentation and discussion of the knowledge regarding oxidant formation, monitoring, transport and modeling in light of the impacts of oxidants in human health and terrestrial ecosystems.

**Nous remercions le Secrétariat des conférences intergouvernementales canadiennes pour les services de traduction simultanée.**

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## NOTE DE L'ÉDITEUR / EDITOR'S NOTE

Les communications sont présentées dans la langue dans laquelle elles ont été données. Un résumé français accompagne les communications de langue anglaise, un résumé anglais les communications de langue française.

The papers are presented in the language in which they were originally given; however, a French abstract accompagnies the English papers while an English abstract accompagnies the French.

# TABLE DES MATIÈRES/TABLE OF CONTENTS

OUVERTURE DE LA CONFÉRENCE/OFFICIAL OPENING PAGE

Jean-Claude Deschênes, sous-ministre
Ministère de l'Environnement du Québec 3

PREMIÈRE SÉANCE/SESSION I
**Les oxydants et leurs effets sur la santé humaine et les écosystèmes terrestres/Oxidants and Effects on Human Health and Terrestrial Ecosystems** 5

Président/Chairman: Dr. Tom Brydges
Service de l'environnement atmosphérique
Environnement Canada

**Le dépérissement de la forêt feuillue du sud-est du Québec: la pollution de l'air est-elle impliquée?** 7

Dr Bernard Bernier
Département des sciences forestières
Université Laval

**Oxidant Induced Effects to Forest Ecosystems: Hidden Injury versus Devastating Forest Declines; Reality versus Conjecture** 21

Dr. John M. Skelly
Department of Plant Pathology
The Pennsylvania State University

**The Effects of Ozone on Individuals and Human populations** 41

Dr. David Bates
Department of Medicine
University of British Columbia

PAGE

DEUXIÈME SÉANCE/SESSION II

**Formation des oxydants/Oxidant Formation** 53

Président/Chairman: Dr Jan W. Bottenheim
Service de l'environnement
atmosphérique
Environnement Canada

**Chemistry of Oxidant Formation: Implications for Designing Effective Control Strategies** 55

Dr. Marcia C. Dodge
Atmospheric Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triang'e Park, USA

**Evaluation of a Surrogate Species Chemical Reaction Mechanism** 79

Dr. Frederick W. Lurmann
Environmental Research and Technology
California

**Ozone Production in Rural Areas** 119

Dr. Jennifer Logan
Department of Earth and Planetary Sciences
Harvard University

**Chemical Considerations in California's Ozone Control Strategy** 123

Dr. John R. Holmes
Research Division
California Air Resources Board

PAGE

**Oxidants for Atmospheric Sulfur (IV)** 124

Dr. Gregory L. Kok
National Center for Atmospheric Research
Boulder, Colorado

**Impacts of Natural Hydrocarbons in Rural Ozone: Modeling and Observations** 137

Dr. Michael Trainer
Aeronomy Laboratory
Environmental Research Laboratories
National Oceanic and Atmospheric Administration
Boulder, Colorado

**TROISIÈME SÉANCE/SESSION III** 151

**Transport et modélisation des oxydants/Oxidant Transport and Modeling** 151

Président/Chairman: Dr. Alan M. Dunker
Environment Science Department
General Motors Research Laboratory
USA

**Design and Applications of the Regional Oxidant Model** 153

Robert G. Lamb
Atmospheric Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park

PAGE

**The Production and Transport of Oxidants during Long Range Transport** 191

Dr. Gregory R. Carmichael
Department of Chemical and Material Engineering
University of Iowa

**Assessment of the Ozone Problem in the New York Metropolitan Area** 215

Dr. S. Trivikrama Rao
Division of Air Resources
New York State Department of Environmental Conservation
Albany, New York

**A Theoretical Study of Regional Oxidant Distribution in North America** 261

Dr. Julius S. Chang
National Center for Atmospheric Research
Boulder, Colorado

**Oxidant Formation and Transport from Petrochemical Complex Emissions in Ontario** 263

Dr. Maris A. Lusis
Air Resources Branch
Ontario Ministry of the Environment

**QUATRIÈME SÉANCE/SESSION 4** 299

**Surveillance des oxydants/Oxidant Monitoring** 299

Président/Chairman: Jean A. Roy
Directeur général du milieu atmosphérique
Ministère de l'Environnement du Québec

PAGE

**The Measurement of Oxidant Precursors and their Relationship to Ozone Formation** 301

William A. Lonneman
Atmospheric Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park

**An Examination of Ozone Levels in Selected Forested Areas of the Eastern United States** 323

Dr. John E. Pinkerton
National Council of the Paper Industry
for Air and Stream Improvement Inc.
New York

**National and Regional Trends in Ambient Ozone and Nitrogen Dioxide Measurements, 1976-1985** 337

William F. Hunt
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standard
Research Triangle Park

**A Review of the Ontario Ozone Problem** 363

Joel Kurtz
Air Resources Branch
Ontario Ministry of Environment

PAGE

**Measurement of Ozone and other Oxidants at Mountains Sites in the Eastern United States** 395

Philip J. Galvin
New York State Department of Environmental Conservation
Division of Air Resources
Albany

**Geographic Variation of Ozone Concentrations at High and Low Elevation Rural Sites in Québec** 411

Robert S. Schemenauer
Atmospheric Environment Services
Donsview, Ontario

**Allocution du ministre de l'Environnement du Québec au dîner offert par le ministère de l'Environnement du Québec** 431

**CONCLUSIONS ET RECOMMANDATIONS/CONCLUSIONS AND RECOMMENDATIONS** 449

Président/Chairman: Jean Piette
Direction des Relations intergouvernementales
Ministère de l'Environnement du Québec

**Effects on Human Health and Terrestrial Ecosystems** 451

Michael Bradley
Executive Director for Coordinated
Air Use Management
Boston

PAGE

**Oxidant Formation** 457

Dr. Kenneth Demerjian
Atmospheric Research Center
State University of New York
Albany

**Oxidant Transport and Modeling** 465

Dr. Philip E. Merilees
Atmospheric Environment Services
Environment Canada

Measurements of Ozone and related Species 471

Dr. Harold I. Schiff
Canadian Institute for Research in Atmospheric Chemistry
York University
Ontario

**ANNEXES/APPENDICES** 479

Programme/Program 482

Liste des participants/List of participants 483

The Decline of the Deciduous Forest in Southeastern Québec: Is Air Pollution Involved (Bernard Bernier, Université Laval, Québec) 499

MOTS DE BIENVENUE/OFFICIAL OPENING

Jean-Claude Deschênes
Sous-ministre
Ministère de l'Environnement du Québec

## MOTS DE BIENVENUE/OFFICIAL OPENING

**Jean-Claude Deschênes**
**Sous-ministre**
**Ministère de l'Environnement du Québec**

Je suis heureux de vous accueillir ici ce matin à trois titres.

Premièrement, d'abord parce que Québec est une ville hospitalière, ouverte et toujours heureuse d'accueillir des visiteurs. Je vous signale d'ailleurs que la ville de Québec a été reconnue l'année dernière par l'UNESCO comme faisant partie du patrimoine mondial. N'est-ce pas là un magnifique symbole de la volonté de conservation qui nous anime?

Deuxièmement, je suis heureux aussi de vous accueillir au nom du ministère de l'Environnement qui, conjointement avec Environnement Canada et le Northeast States for Coordinated Air Use Management, a organisé et parrainé le symposium scientifique qui débute ce matin. Faut-il rappeler d'ailleurs l'importance que le Québec accorde aux questions environnementales et particulièrement celles reliées à la qualité de l'air. C'est en effet ici même, il y a deux ans qu'un symposium semblable eut lieu concernant cette fois les précipitations acides.

Troisièmement, nous sommes très heureux d'accueillir une assemblée nombreuse et hautement spécialisée car la connaissance est la première des clés requises pour assurer la protection de notre qualité de vie. Les échanges de connaissances qui auront lieu au cours des prochains jours seront sûrement stimulants, car de tels échanges constituent la base même des progrès de notre cause commune, la qualité de l'environnement.

Un symposium n'est toutefois pas une fin en soi car il s'agit d'un moyen. C'est un moyen d'accroître nos connaissances et d'enrichir notre compréhension des phénomènes liés à la nature et à la vie. Nous oeuvrons tous sur de l'essentiel car la qualité de l'air est indispensable à toute forme de vie. Au point de vue des finalités de nos actions respectives, il faut aussi rappeler que la population attend beaucoup des organismes et institutions ministérielles pour améliorer le présent et garantir l'avenir.

Deux sondages récents au Québec attestent de cette volonté de la population. Dans le premier sondage effectué à l'automne 1985 sur la perception de la population à l'égard du concept de la qualité de la vie, la qualité de l'air est ressortie comme le premier élément (42 pour cent) constituant de cette notion large qu'est la qualité de la vie. Dans un second sondage effectué pour connaître la perception de la population à l'égard des priorités concernant les champs de la recherche, la population a indiqué que la recherche en santé et la recherche dans le domaine de l'environnement constituent les toutes premières priorités, la santé recueillant 87 pour cent des votes et l'environnement 82 pour cent.

En conclusion, une telle convergence de vos travaux et de la perception de la population, constitue des garanties que nous réussirons à améliorer et à garantir pour les générations à venir, un air sain et une qualité de vie à laquelle tous aspirent.

Je vous souhaite donc la bienvenue à ce symposium et le plus grand des succès à vos délibérations des prochains jours.

PREMIÈRE SÉANCE/SESSION I

LES OXYDANTS ET LEURS EFFETS SUR LA SANTÉ HUMAINE ET LES ÉCOSYSTÈMES TERRESTRES/OXIDANTS AND EFFECTS ON HUMAN HEALTH AND TERRESTRIAL ECOSYSTEMS

Président/Chairman

Dr Tom Brydges
Service de l'environnement atmosphérique
Environnement Canada/Atmospheric Environment Service
Environment Canada

# LE DÉPÉRISSEMENT DE LA FORÊT FEUILLUE DU SUD-EST DU QUÉBEC: LA POLLUTION ATMOSPHÉRIQUE EST-ELLE IMPLIQUÉE?

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# The Decline of the Deciduous Forest in Southeastern Québec: is Air Pollution Involved?

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## Abstract

The deciduous forest of southeastern Québec is dominated by sugar maple (Acer saccharum Marsh.). This species and some of its associated species are declining at an alarming rate at several rural locations since 1980. The study area, located south of the St.Lawrence River and mainly in the Appalachians between Québec City and the State of Maine, covers about 17 000 km². A study on the foliar nutrient status of a great number of maple stands in this region since 1983 revealed widespread deficiencies of phosphorus (P) and more noticeably potassium (K) in the declining sugar maple stands. The deficiencies are accompanied by visual symptoms[1] that are probably unique to the current decline situation. To our knowledge, they have not been reported in previous declines in the deciduous forest of northeastern North America. Nutrient deficiencies have developed in recent years and we believe they play a key role in the forest decline by constituting a decisive predisposing, or inciting, stress factor. The origins of these nutrient disturbances are discussed in the light of several hypotheses that examine the effects of air pollution on forests.

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*1 The illustration of foliar symptoms (not shown in this text) is emphasized in the presentation.*

# Le dépérissement de la forêt feuillue du sud-est du Québec: la pollution atmosphérique est-elle impliquée?

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## 1. Résumé

La forêt feuillue du sud-est du Québec est dominée par l'érable à sucre (Acer saccharum Marsh.). Cette essence et quelques essences compagnes dépérissent d'une façon alarmante dans plusieurs localités rurales depuis 1980. Le territoire étudié couvre quelque 17,000 km² au sud du St-Laurent, principalement dans les Appalaches, entre la ville de Québec et la frontière américaine du Maine. Un inventaire du statut nutritif conduit dans un grand nombre d'érablières de ce territoire depuis 1983 a révélé l'existence étendue de carences en phosphore (P) et surtout en potassium (K) dans les érablières en voie de dépérissement. Ces carences s'accompagnent de symptômes[1] qui sont vraisemblablement spécifiques à la situation actuelle du dépérissement, n'ayant pas, à notre connaissance, été rapportés dans des cas antérieurs de dépérissement de la forêt feuillue dans le nord-est américain. Elles se sont développées au cours des récentes années et on croit qu'elles jouent un rôle clé dans le dépérissement de la forêt. L'approvisionnement insuffisant en éléments nutritifs peut constituer un facteur de stress prédisposant décisif. L'origine de ces perturbations de nutrition est discutée à la lumière des diverses hypothèses émises sur les effets de la pollution atmosphérique sur la forêt.

## 2. Introduction

La forêt feuillue du sud-est du Québec est présentement en proie à un dépérissement progressif inhabituel depuis le début de la

*1 L'illustration des symptômes foliaires (non reproduits ici) occupe une place centrale dans cet exposé*

présente décennie. Des relevés récents montrent que l'érable à sucre, essence dominante de cette forêt, est en déclin dans une large partie de son aire de distribution au Québec (Bordeleau, 1986; Carrier, 1986).

Bien qu'il existe beaucoup de variation dans le niveau de dépérissement de la forêt à l'échelle du territoire, le phénomène est en progression marquée et il est une cause d'inquiétude croissante (Carrier, 1986; Robitaille, 1986).

La production de sirop d'érable est une tradition séculaire au Québec et l'aménagement de l'érablière à cette fin a connu très peu de transformations récentes, si ce n'est l'introduction du système de vacuum pour la récolte de la sève brute qui remonte au début des années 1970. Beaucoup de propriétaires d'érablière ont toutefois conservé l'exploitation traditionnelle aux seaux, et on sait aujourd'hui que le mode d'exploitation de l'eau d'érable ne peut être retenu comme une cause du dépérissement de la forêt (Carrier, 1986).

Parmi les stress biotiques et abiotiques qu'a subis la forêt depuis les dix dernières années, il faut signaler de sévères défoliations par la livrée des forêts (Malacosoma disstria) au début des années 1980, surtout dans la partie sud du Plateau des Appalaches (Lachance et al., 1984), et des conditions climatiques exceptionnelles, dont une sécheresse marquée en 1983. Ces stress naturels ont sans doute contribué à la mortalité des arbres dans plusieurs érablières, mais ils sont incapables, à eux seuls, d'expliquer le présent phénomène de dépérissement, qui a commencé dans certaines localités avant les années 1980 et qui est en progression dans les régions qui ont totalement échappé aux défoliations par les insectes.

## 3. Les symptômes associés au dépérissement

3.1 Symptômes généraux. Les symptômes généraux du dépérissement de la forêt feuillue du sud-est du Québec ne diffèrent pas fondamentalement de ceux qui ont été rapportés dans des cas antérieurs de

dépérissement et attribués à des causes naturelles (Sinclair, 1964): réduction de la croissance des rameaux, qui donne naissance à des touffes de feuilles; réduction de la croissance radiale des tiges, qui s'observe facilement chez l'érable à sucre par la lenteur de cicatrisation des entailles; réduction de la taille des feuilles, qui confère à la cime un caractère aéré; mortalité des rameaux et des petites branches qui ne survivent pas à la période hivernale, suivie de la mortalité de branches plus grosses l'année suivante; formation de rameaux adventifs sur le tronc et les grosses ramifications, accompagnant la mortalité des branches; invasion des grosses racines par l'Armillaire, pathogène racinaire normalement tenu en échec lorsque l'arbre est vigoureux. D'autres traits observés antérieurement, comme la détérioration des racines fines et l'épuisement progressif des réserves organiques, sont présumément aussi applicables à la situation actuelle parce qu'ils sont des manifestations du mauvais fonctionnement général de l'arbre et qu'ils accompagnent les autres perturbations (Sinclair, 1964).

Bien que ces symptômes soient facilement observables dans la forêt dépérissante au Québec, ils ne sont pas spécifiques à une cause particulière et, en conséquence, ne peuvent être utilisés pour identifier un facteur causal. Cependant, en plus de ces symptômes généraux, il en existe d'autres que nous croyons être spécifiques à la situation présente parce que, à notre connaissance, ils n'ont jamais été rapportés dans les cas antérieurs de dépérissement de la forêt naturelle dans le nord-est américain.

3.2 Symptômes spécifiques: un outil de diagnose. En discutant du phénomène du dépérissement de la forêt, Prinz (1985) a souligné avec à propos que pour en expliquer la cause, il faut satisfaire aux trois conditions suivantes:

(a) on doit pouvoir relier tous les symptômes spécifiques du dépérissement au facteur causal en question;

(b) le développement du dépérissement dans le temps doit coïncider avec celui du facteur causal, en tenant compte des effets cumulatifs;

(c) la distribution spatiale du dépérissement doit coïncider largement avec la distribution du facteur causal.

Dans le cas du dépérissement de la forêt feuillue au Québec, les éléments pouvant satisfaire à ces conditions ne sont pas tous réunis, mais la symptomatologie foliaire spécifique à la forêt dépérissante est de mieux en mieux connue. Cet aspect est essentiel car la première condition suppose une connaissance adéquate des symptômes spécifiques au dépérissement. De plus, sur cette connaissance repose une bonne partie de l'information nécessaire pour rencontrer les autres conditions posées par Prinz (*loc.cit.*). Pour cette raison, le gros de cette présentation portera sur l'illustration des symptômes foliaires les plus répandus dans les érablières dépérissantes.

Certains de ces symptômes, comme le port dressé des feuilles et leur couleur vert sombre, peuvent servir de signes avant-coureurs du dépérissement parce qu'ils précèdent les premières manifestations de mortalité des rameaux. Les symptômes typiques de carences minérales qui les suivent, et qui sont caractéristiques de la forêt dépérissante, sont, selon nous, spécifiques à la situation actuelle. Dans la région étudiée, ces symptômes de carence sont principalement ceux de K ou de P ou des deux éléments à la fois. Ces carences ne se sont développées qu'au cours des toutes récentes années. Leur existence met en lumière un sérieux problème de déséquilibre nutritif suggérant que ce stress joue vraisemblablement un rôle majeur dans le dépérissement de la forêt.

## 4. Carences nutritives et dépérissement

Avant d'évoquer les causes possibles de ces perturbations de nutrition, il importe de se demander si les carences nutritives observées sont une cause ou une conséquence du dépérissement. Trois

raisons nous incitent à rejeter l'hypothèse qu'ils en soient une conséquence:

(a) à notre connaissance, ils n'ont jamais été rapportés dans des cas antérieurs de dépérissement de la forêt feuillue dans le nord-est américain;

(b) il est vrai qu'une partie importante de la forêt feuillue du sud-est du Québec a subi des défoliations sévères par les insectes qui se sont produites deux ou trois années consécutives, ce qui peut affecter significativement le cycle nutritif et causer ou accentuer le dépérissement (Bernier et al., 1985). Cependant, les symptômes de carences nutritives observés sont les mêmes, que la forêt ait été ou non défoliée par les insectes;

(c) le statut nutritif déséquilibré de la forêt peut être restauré par une application appropriée d'engrais qui fait aussi disparaître les symptômes de carences nutritives (Bernier et Brazeau, en prép.).

La carence en K dans le territoire étudié est un phénomène répandu, confirmé par trois années d'étude du statut nutritif foliaire dans un grand nombre de stations du territoire; elle est plus répandue que la carence en P (Bernier et Brazeau, en prép.). Mais celle-ci demeure un des traits saisissants de plusieurs érablières dépérissantes des Basses-Terres du St-Laurent et des Appalaches. Ces symptômes s'accompagnent d'une sénescence foliaire hâtive et du déclin de la cime des arbres.

La situation comporte des similitudes et des différences avec le dépérissement de la forêt observé en Europe centrale. En effet, plusieurs chercheurs ont aussi mis en lumière l'existence de carences nutritives associées au dépérissement de la forêt en Allemagne (Huettl, 1986; Rehfuess, 1980, 1983; Zöttl, 1985a, 1985b; Zöttl et Huettl,

1985) et ils attribuent un rôle majeur à la perturbation de nutrition dans plusieurs cas récents de dépérissement de la forêt. Les différences viennent surtout de la nature des carences observées: les carences en Mg sont répandues en Allemagne alors qu'elles ne sont pas ou peu impliquées dans la région de la forêt feuillue du sud-est du Québec que nous avons étudiée. Par ailleurs, à notre connaissance, on n'a pas rapporté de cas de carences en P dans les forêts dépérissantes d'Europe centrale.

## 5. La pollution atmosphérique est-elle à l'origine de ces perturbations de nutrition?

Si l'on revient aux trois conditions posées par Prinz (1985) pour expliquer les causes du dépérissement, on peut affirmer, en ce qui a trait au premier point, qu'il existe vraisemblablement des symptômes spécifiques au dépérissement de la forêt feuillue au Québec, dont on connait la nature sans pour autant connaître encore précisément la genèse. Ce qui semble certain, c'est qu'on assiste à des perturbations majeures du cycle des éléments qui font probablement intervenir plusieurs des hypothèses émises sur les rôles de la pollution atmosphérique sur le dépérissement de la forêt, lesquels ont fait l'objet de revues récentes (Evans, 1982; Kozlowski et Constantinidou, 1986; McLaughlin, 1985; Guderian et al., 1985; Morrison, 1984; Roberts, 1984). Ceux-ci incluent: 1) le lessivage accru des cations basiques au-delà de la zone d'enracinement par excès d'anions d'origine anthropique (Foster, 1985; Huettl, 1986; Johnson et al., 1985); 2) l'acidification du sol sous l'influence des dépôts acides, pouvant solubiliser les métaux lourds susceptibles d'intoxiquer les racines fines (Ulrich, 1983) et de gêner la nutrition en P; 3) un surplus de $NO_3^-$ d'origine anthropique pouvant créer une demande accrue pour les autres éléments et affecter le système mycorhizateur (McLaughlin, 1985) dont le rôle en nutrition est bien connu, notamment pour l'acquisition de P; 4) le pluvio-lessivage foliaire accru sous l'influence des dépôts acides et

des photooxydants (Cronan; 1984, Guderian et al., 1985; Scherbatskoy et Klein, 1983; Skeffington et Roberts, 1985; Wood et Bormann, 1975; Zöttl, 1985a). Ce dernier point semble particulièrement pertinent pour K en raison de son abondance dans la solution apoplasmique foliaire et du fait qu'il n'est pas incorporé dans les structures organiques. Miller (1984) est d'avis que les mécanismes de remplacement des pertes occasionnées par les brouillards acides sont suffisamment rapides pour restaurer les pools foliaires, à moins que les tissus soient affectés par d'autres stress tels que l'ozone.

Ouvrons ici une parenthèse pour apporter la rectification suivante: lors d'un colloque antérieur sur le dépérissement de l'érablière au Québec, nous avons affirmé que des lésions foliaires causées par l'ozone étaient associées aux symptômes de carences nutritives (Bernier et Brazeau, 1986). Nous avons fait une erreur d'interprétation: les lésions foliaires présumément attribuées à l'ozone sont beaucoup plus limitées qu'anticipé. Cependant, ceci n'élimine pas la possibilité d'une action subtile, asymptômatique, des oxydants, comme cela a été observé dans le nord-est américain (Wang et al., 1986).

Quant aux deux autres conditions posées par Prinz (1985), on ne peut spéculer sur la coïncidence dans le temps et l'espace du dépérissement avec le facteur causal, celui-ci n'étant encore qu'hypothétiquement connu. Ce que l'on sait, cependant, c'est que là où la forêt est dépérissante, les symptômes de carences nutritives évoqués plus haut sont présents, ce qui permet de présumer que la distribution spatiale du dépérissement coïncide avec la distribution du facteur incitatif.

Le sud-est du Québec est une des régions les plus sévèrement polluées au Canada: les dépôts annuels de $SO_4^{2-}$ et de $NO_3^-$ sous forme humide seulement s'élèvent à 40-60 kg $ha^{-1}$ et 10-30 kg $ha^{-1}$, respectivement (Rennie, 1986). Les concentrations d'ozone sont largement in-

connues, si ce n'est les observations de Maltais et Archambault (1985) pour une année où les concentrations mesurées variaient de 80-150 nL $L^{-1}$ dans la zone rurale des Basses-Terres du St-Laurent. Plusieurs sols du territoire étudié sont intrinsèquement pauvres en K, en particulier dans la ceinture qui entoure le complexe ophiolitique de la région de Thetford Mines. C'est dans cette région que le dépérissement est le plus sévère (Bordeleau, 1986). Cependant, les carences en K ne sont pas limitées à cette région mais, d'une façon générale, se rencontrent à des degrés divers dans l'ensemble du territoire inventorié, lequel renferme une grande diversité de formations géologiques (St-Julien et Hubert, 1975) et de sols (Baril, 1974). De même, les carences en P sont sporadiquement présentes dans tout le territoire étudié (Bernier et Brazeau, en prép.).

L'étude du statut nutritif foliaire et la mesure des pools d'éléments disponibles du sol indiquent que le statut foliaire de P est corrélé au pool de P disponible de la couverture morte alors que K foliaire est corrélé au pool de K échangeable des horizons minéraux de surface (Bernier et al., 1985). Ces observations suggèrent que des modifications de la chimie du sol dans la zone prospectée par les racines fines pourraient avoir entraîné une réduction progressive de la disponibilité des éléments, un aspect qui semble supporté par les observations de Cagnon et al. (1986). Comme le feuillage est carencé en P et K, la translocation saisonnière de ces éléments est affectée et leur restitution par la litière est anormalement faible (Bernier et Brazeau, en prép.), introduisant ainsi un cercle vicieux dans le cycle des éléments à l'intérieur de l'écosystème.

## 6. Conclusion

Les observations rapportées ici suggèrent que les carences nutritives jouent probablement un rôle majeur direct dans le dépérissement de la forêt, comme cela a aussi été rapporté en Europe centrale (Guderian et al., 1985; Zöttl et Huettl, 1985). Ceci peut être causé

par des niveaux réduits des réserves d'éléments disponibles dans la zone d'enracinement ou -- dans le cas du potassium du moins -- par lessivage accru du feuillage, ou par d'autres perturbations encore mal définies du cycle des éléments. De telles modifications sont présumées résulter de stress anthropiques et la situation nécessite avec urgence des recherches additionnelles pour préciser l'origine du phénomène.

## 7. Remerciements

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# OXIDANT INDUCED EFFECTS TO FOREST ECOSYSTEMS: HIDDEN INJURY VERSUS DEVASTATING FOREST DECLINES: REALITY VERSUS CONJECTURE

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## RÉSUMÉ

Des statistiques datant de 1975-1984 sur l'exposition à l'ozone pour la plupart des États-Unis ont été récemment présentées dans divers rapports. De ces derniers, on retient qu'il existe encore bien des divergences d'opinions concernant l'influence sur la végétation des périodes d'exposition de pointe par rapport aux périodes d'exposition saisonnière, à long terme. Des dommages occasionnés par l'ozone ont été observés chez diverses espèces forestières partout aux États-Unis. Les symptômes visibles comprennent une légère chlorose, des changements dans la pigmentation, la nécrose et, dans certains cas, une réduction de la croissance, puis la mortalité. Ces symptômes sont très souvent associés à des épisodes d'$O_3$; seules les mouchetures à la surface supérieure des feuilles en fin d'été et la coloration prématurée en automne semblent échapper à ce phénomène. Même les doses saisonnières d'ozone peuvent apporter des changements aussi subtils que la croissance réduite sans toutefois qu'il y ait de symptômes foliaires apparents. Le stress provoqué par l'ozone peut éventuellement accroître la réaction des végétaux touchés à d'autres agents biotiques et abiotiques. Cependant, à l'échelle régionale, les statistiques récentes sur l'exposition à l'ozone ne laissent paraître aucune preuve de la présence de concentrations d'ozone suffisantes pouvant causer le déclin catastrophique des forêts régionales. D'autres causes directes (dont la sécheresse, le zigzag (Porthètria dispar), la livrée, Armillariella mellea) ont par le passé joué un rôle d'instigateur dans le déclin régional des arbres (et des forêts).

# Oxidant Induced Effects to Forest Ecosystems: Hidden Injury Versus Devastating Forest Declines; Reality Versus Conjecture

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## Abstract

Ozone exposure statistics for much of the United States for the period 1975-1984 have been presented in several recent reports. Considerable debate exists concerning the influence of peak exposure periods versus longer term seasonal exposure periods on subsequent vegetation responses. Ozone induced foliar injury has been observed on numerous indigenous forest species throughout the USA. Recorded visible symptoms include mild chlorosis, pigmentation changes, necrosis, and in some instances, growth decline and mortality. Such visible symptoms have most often been associated with peak episodes of $O_3$ exposures; exceptions may be late summer stippling of upper leaf surfaces and premature fall colorations. Seasonal ozone doses may be sufficient to induce more subtle changes as manifested by reduced growth without the presence of visible foliar symptoms, i.e., the phenomenon of "hidden injury." Ozone induced stress may subsequently lead to increased responses of affected plants to other abiotic and biotic agents. However, on a regional basis, recent ozone exposure statistics do not present evidence of sufficient ozone concentrations to cause cataclysmic types of regional forest declines. Other direct causal agents (i.e., drought, gypsy moth, forest tent caterpillar, Armillariella mellea) have historically been shown capable of inciting regional tree (forest) declines.

Ozone Exposure Statistics:

Until the mid to late 1970s, there was little reliable ozone data available from rural sites. With the exceptions of studies done in the forested areas of Ontario (Linzon, 1960) and in the mountains and valleys of Tennessee and West Virginia (Berry and Ripperton, 1963; Berry, 1964), the San Bernardino Mountains of California (Miller, 1982), and the Blue Ridge Mountains of Virginia (Skelly et al., 1980, 1984) there has been little attention given to ambient ozone doses in remote areas. Information on effects of photochemical oxidants on forest trees and forest ecosystems is likewise insufficient. Evidence of broader scale vegetation effects, especially in rural agricultural areas, and the interests of the various federal agencies (U.S. Environmental Protection Agency; U.S. Department of Interior, National Park Service; U.S. Department of Agriculture, Forest Service; and others) spurred more elaborate use of the USEPA's air quality monitoring and data storage system termed Storage And Retrieval Of Aerometric Data (SAROAD) to determine pollutant loadings. Much of the historic SAROAD data base has dealt with metropolitan statistical areas but hourly data exists since 1978 for more than 350 individual sites that have been designated as rural or remote (NCASI, 1982; Pinkerton and Lefohn, 1986; USEPA 1986a, b). Temporal trends in $O_3$ concentrations under urban conditions for the period 1975-1983 have varied. The years of 1981 and 1982 experienced the lowest recorded values (Figure 1). Seasonal (April-September; 0900-1600 h) $O_3$ values ranged from 0.043-0.050 ppm.

On a national basis, rural areas experienced about 10 percent of all days with at least one hour in excess of 0.08 ppm $O_3$. Seasonal 7 hour averages (0900-1600 h) ranged from 0.021 to 0.050 ppm $O_3$ with a mean of 0.044 ppm $O_3$. Highest monthly averages occurred in May, July, and August for all rural sites with highest values ranging from 0.023 to 0.071 ppm $O_3$; average values were 0.053 ppm $O_3$.

Pinkerton and Lefohn (1986) examined ozone concentration data from the 1983 SAROAD data base for 12 southeastern states involved in commercial timber production. Exposure statistics for an April-October, 7 hour (0900-1600 h) seasonal mean indicate that a slightly higher exposure (range 0.032-0.058 mean = 0.048 ppm $O_3$) exists in that area of the country when compared to national data (0.044 ppm $O_3$ h seasonal).

Peak ozone concentrations as recorded in data sets available from the National Air Pollution Background Network have been presented in Figure 2 (USEPA, 1986a). At these sites about 6 percent of the recorded 3 year collective highest 1-hour $O_3$ concentrations were less than 0.10 ppm and fewer than 20 percent of the values were higher than 0.12 ppm.

The USEPA (1986a) concluded from an analysis of available data that non-urban (i.e., remote) areas may sometimes sustain higher peak ozone concentrations than those concentrations found in urban areas. A second USEPA (1986b) report concluded, however, that longer term seasonal $O_3$ averages of 7 or 12 hours daily daylight time periods in remote areas appear to be similar to those monitored in urban areas.

The latter report (USEPA, 1986b) also suggested that "serious consideration should be given to setting a long term standard in the range of 0.04-0.06 ppm $O_3$ to protect crops as well as trees and other native vegetation. The level of such a standard will be influenced by the protection from long-term exposures of concern afforded by the 1-hour standard."

Ozone Induced Effects:

The conceptual model as developed by Tingey and Taylor (1982) perhaps best illustrates the role air pollutants can play in determining plant health (Figure 3). Although this model was developed to demonstrate differing levels of physiological and biochemical process disturbances, a similar tact can be used to illustrate whole plant and

even ecosystem level responses (Figure 4). The response of an individual tree, forest stand, or entire ecosystem will depend upon the initial health of the system to be perturbed, the initial exposure dose of the pollutant, factors governing the opportunity for homeostasis to occur (including a continuing pollutant dosing) and the presence of related environmental stress factors including abiotic and biotic agents. In fact, if homeostasis is allowed to near completion within individuals once perturbed then detection of any induced effects may be quite difficult to "tease out" of a diverse and biologically variable system such as a forest ecosystem.

Notable occurrences of ecosystem level devastations (Sudbury, Ontario, CAN; Copper Hill, TN, USA) have occurred from point source emissions of $SO_2$ and heavy metals. Changes in forest tree species composition have occurred in the San Bernardino Mountains of California following long-term exposures to high doses of ozone and its precursors transported from the Los Angeles basin area (Miller et al., 1982). More subtle changes in genetic tolerances may be taking place in the Blue Ridge Mountains of Virginia as illustrated in reduced growth rates of foliarly sensitive eastern white pines (Figure 5) (Benoit et al., 1982).

Visible foliar injuries due to ozone have been described and pictorially displayed in numerous references (Jacobson and Hill, 1970; USEPA, 1976; Skelly and Lambe, 1974; Skelly et al., 1987). With the exceptions of adding new species to the listings of symptomatic plants (e.g., Davis and Umbach, 1981; Duchelle and Skelly, 1981) little has changed from initial descriptions of injury offered by earlier researchers. Broadleaf foliar responses include upper leaf surface stippling (pigmentation changes), chlorotic spotting, chlorotic mottling, bifacial necrotic lesions, and premature leaf coloration leading to early senescence. Visible symptoms in conifers include chlorotic spotting or mottling of current or more commonly of older needles, loss of older needles, and tip-burn of young needles if the

pollutant exposure period coincides with needle emergence. Short needles may also be commonly found on more sensitive pines following years of accumulative exposure responses.

Following an analysis of 18 studies which related foliar injury to exposure dose, the USEPA (1986a) summarized visible foliar injury threshold doses; i.e., foliar injury was considered to be unlikely at ozone doses below these figures for trees and shrubs:

$O_3$ at 0.20 to 0.51 ppm for 1 hour

$O_3$ at 0.10 to 0.25 ppm for 2 hours

$O_3$ at 0.06 to 0.17 ppm for 4 hours

Therefore, injury threshold doses, when compared to actual exposure doses recorded at remote sites suggest that foliar injury should not be evident except on the most sensitive species. A recent survey by Davis and Bennett (1985) provides support to this conclusion in that the predominant species marked with ozone symptoms in four Mid-Atlantic National Park Service areas were sensitive-bioindicator type species such as native black cherry, tulip poplar, common milkweed, flowering dogwood and native grape. Injury was not as common on white ash, redbud, witch hazel and sassafras. They also noted that foliar injury due to insects and disease causing pathogens occurred throughout the survey area.

The amount of ozone dose needed to induce foliar injuries on sensitive plants is much better understood than are the threshold doses needed to induce growth and yield effects (with or without foliar injuries). Correlations between degrees of foliar injuries and subsequent yield losses are not well defined (USEPA, 1986a). The obvious obstacle to clarifying this most important need is our current inability to discern differences in productivity within in-situ forest stands which have closed canopies and which exist under ambient regional ozone exposure conditions, i.e., we have no natural control sites.

Hidden Injury - Perhaps the most significant effect of regional episodic and longer term seasonal average ozone exposures lies just below the "no perceptable effects" line presented in Figure 4. The hidden injury concept of plant damage was developed by Stoklasa (1923). He associated hidden injury with: 1) a reduction in photosynthesis, 2) premature senescence, 3) an accumulation of sulfates, 4) an overall unthrifty appearance of the vegetation without actual lesions on the leaves, 5) reduced growth and yield, and 6) increased susceptibility to disease. Thomas (1956) reviewed the literature on hidden injury and further defined hidden injury as interference with growth, photosynthesis, respiration, reproduction, enzymatic function, or a demonstrable increase in susceptibility to disease without lesions or discolorations on the leaves, stems or roots of plants. He determined that hidden injury had occurred from the impact of oxidant pollution.

Keller (1977) initiated the term "latent injury" to replace hidden or invisible injury. Latent injury included all forms of injury to plants which were not accompanied by symptoms discernible to the naked eye and thus included any physiological disorder, reversible or irreversible, whether or not it lead to a growth reduction or impairment of sexual reproduction. Keller subjected silver fir to 0.1 ppm $SO_2$ for 10 weeks and found significant reductions in photosynthesis without the appearance of visible symptoms. Trimble (1980) and Kress (1978) have prepared comprehensive literature reviews regarding this subject.

Growth depressions without accompanying foliar injuries in forest trees have been reported in numerous laboratory, greenhouse, and controlled field exposure studies. (Numerous citations may be found in USEPA, 1986a.) One of the more recent investigations conducted under field conditions using ambient ozone exposure doses was conducted in the Blue Ridge Mountains of Virginia (Duchelle et al., 1982, 1983; Skelly et al., 1982, 1984). Three investigations were conducted within open-top chambers used to exclude ozone; two dealt with effects of filtered air

on foliar biomass production of native plants and a third dealt with effects on forest tree seedlings that had been transplanted into the respective chambers.

The effect of ambient ozone ($O_3$) on biomass production of native vegetation was examined during a 3-year study (Duchelle et al., 1983). Twelve 3 m diameter plots were established in spring, 1979, with four replicates each receiving charcoal filtered air and non-filtered air via open top chambers, and four replicates receiving ambient air in open plots. Total above-ground biomass was harvested twice each growing season (1979, 1980, 1981) at approximately mid-season and in early fall. In each year, biomass was greatest in the filtered air chambers. The total 3-year cumulative dry weight for the treatments was significantly different ($P<0.05$) with 1.38, 1.09 and 0.89 kg $m^{-2}$ in the filtered, non-filtered and open plots, respectively. In a second foliar biomass experiment, conducted only during the 1980 season, fifteen 0.25 $m^2$ circular microplots were established within each of six additional 3 m diameter plots. The vegetation within subsets of these microplots was harvested at different intervals during the growing season. In three out of six phases of this study, the total above-ground biomass of native vegetation was the largest in charcoal filtered air compared with the ambient air treatments.

Open top chambers were also used to test the effect of ambient doses of the pollutant on the growth of 8 planted forest tree species native to the area (Duchelle et al., 1982). Height growth was suppressed for all species at the end of the second growing season when grown in open plots (no chamber) and ambient chambers compared to those grown in charcoal-filtered air supplied chambers. Height growth trends of open < ambient chamber < filtered air chamber were consistent. Virginia pine and green ash were significantly taller ($p=0.10$) when grown within filtered air chambers. Tulip poplar and green ash manifested purple stippling on the adaxial leaf surface and sweetgum

developed purple coloration under open or ambient chamber conditions; other species exhibited no visible injury.

These three investigations are significant when the ozone exposure doses are examined (Table 1) and then related to more regional exposure doses as reviewed elsewhere in this paper.

Ozone and Forest Declines

Initial reports of a "new type" of forest decline as reported to be occurring in the Black Forest of West Germany (Prinz et al., 1982) spurred closer looks at tree health in forests of the United States and Canada. Major concern has emerged over observed declines of high elevation spruce and fir forests (Johnson, 1983), various pine species of the Southeast (Sheffield et al., 1985), and sugar maple throughout the northeast United States and southeastern Canada (McIlveen et al., 1986). Among many possible causal agents, anthropogenic air pollutants are being closely examined for any possible role they may play in these phenomena (USEPA, USDA-FS, 1986). The major policy question being addressed by the National Acid Precipitation Assessment Program-Forest Response Project queries--Is there a significant problem of forest damage in North America which might be caused by acidic deposition, alone or in combination with other pollutants? Ozone sulfates, nitrates, and associated acidic precipitation are obvious suspects under investigation.

Ozone, at current ambient regional doses, does not appear to be a single etiological agent capable of directly inciting the observed forest tree declines. Ozone may however, be at sufficient doses to induce subtle growth changes within an individual without the presence of visible foliar symptoms. Such "hidden injury" will obviously be difficult to detect since all individuals within a population are exposed to very similar daily, seasonal, or yearly doses. The predispositioned role of ozone leading to increased disease and insect

attack of affected trees remains to be determined. Evidence for this phenomenon exists (James et al., 1980; Skelly, 1980).

However, it is critically important for us to also recognize that "forest declines" have occurred on an historical basis. We must accept that several abiotic and biotic agents are capable of independently inciting devastating declines and mortalities and still other agents work in more clandestine fashions to cause slowdowns in growth leading to eventual declines and even mortalities. Abundant literature exist on the historical and more current attack occurrences of respective forest species as illustrated by the balsam woolly adelgid, gypsy moth, forest tent caterpillar, saddled prominent, Armillariella mellea, Heterobasidion annosum, and various leaf invading fungi. Literature pertaining to major historically important declines of forest trees throughout the Northeast U.S. is being reviewed (USDA-FS, 1987). Abiotic stresses, limiting site variables, and all possible biotic and abiotic interactions must be taken into account when attempting to ascribe a cause and effect role for additional stress agents such as anthropogenic pollutants. Our challenge is to carefully evaluate effects of pollutant depositions which occur in concert with natural forest (ecosystem) processes. Many of these stress inducing agents do not need the additional influences of anthropogenic air pollutants in order to cause the demise of an entire species within a specific geographical area.

A brief excert from the Third Annual Report of the Pennsylvania Department of Agriculture, Part II-for the year 1897 follows:

> "Almost all of native red and black spruce in eastern Sullivan and western Wyoming counties (of Pennsylvania) were killed between 1880 and 1896 with the greatest destruction occurring during 1894-1896. This area was the last stand of spruce in Pennsylvania. This destruction was caused by a number of species of spruce bark

beetles belonging to the Scolytidae (species were given). By 1896 the spread of the insects had stopped." (Pa. Div. For., 1897)

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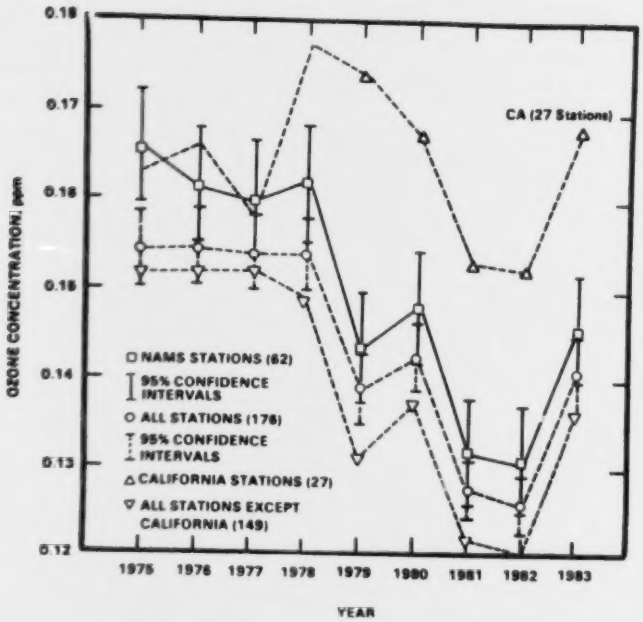


Figure 1. National trend in composite average of the second highest value among daily maximum 1-hour ozone concentrations at selected groups of sites, 1975 through 1983 (USEPA, 1986a).

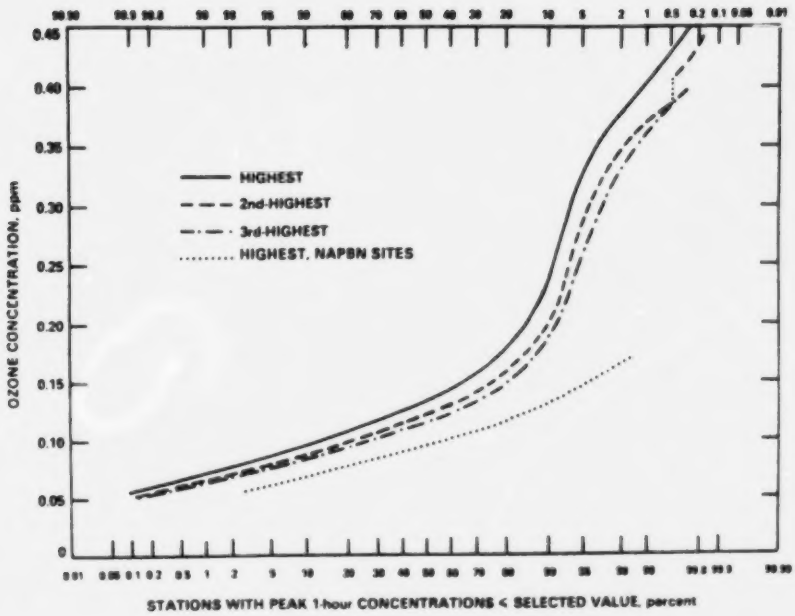


Figure 2. Distributions of the three highest 1-hour ozone concentrations at valid sites (906 station-years) aggregated for 3 years (1979, 1980, and 1981) and the highest ozone concentrations at NAPBN sites aggregated for those years (24 station-years) (USEPA, 1986a).

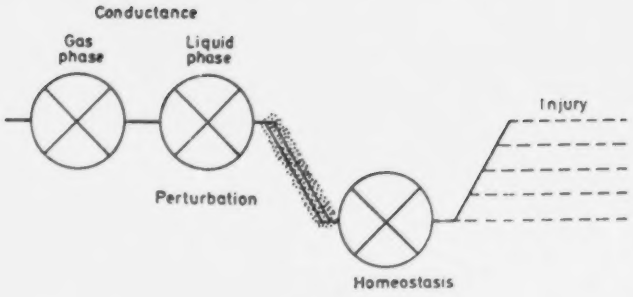


Figure 3. Conceptual model of the physiological and biochemical processes controlling plant response to ozone. Major processes include conductance (gas and liquid phases) and homeostasis. (From Tingey and Taylor, 1982).

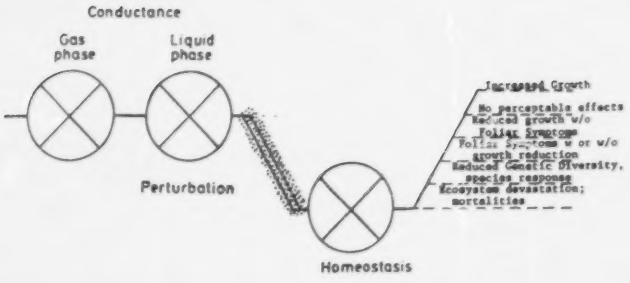


Figure 4. The Tingey and Taylor (1982) model modified to relate similar basic physiological and biochemical whole plant responses to pollutant induced changes in forest systems.

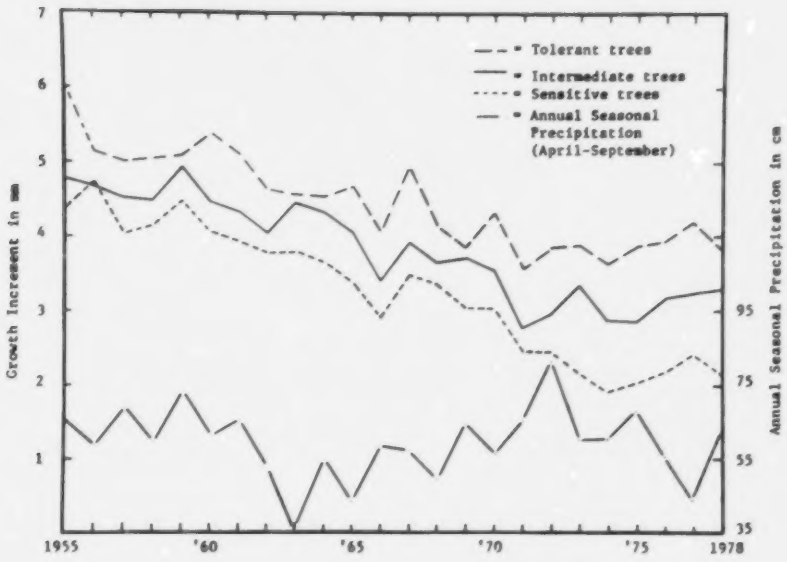


Figure 5. Radial increment growth of eastern white pine in various sensitivity classes as measured by foliar injury due to ozone exposure in the Blue Ridge Mountains of Virginia (10 dominant or co-dominant trees/class) (Benoit et al., 1982). Several of the sensitive trees have since died and were found infected by Verticicladiella procera (Skelly, 1980).

# THE EFFECTS OF OZONE ON INDIVIDUAL AND HUMAN POPULATIONS

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## INTRODUCTION

A full understanding of our contemporary knowledge of the effects of ozone on the lung, requires consideration of a large body of animal inhalational toxicology, of the acute effects of controlled human exposure, and of the four or five relevant epidemiological studies. These are the topics treated in the Criteria Documents published by the Environmental Protection Agency of the USA; the volumes on ozone have just been published[1]; and anyone needing more detailed information should begin by consulting them. In this summary, only human exposures and epidemiological data will be discussed.

## CONTROLLED HUMAN EXPOSURES

These studies, initiated twenty years ago, permit measurement of the acute effects of gases on subjects at rest or during exercise. They have contributed a great deal to our understanding of the dose response relationship. The present results may be summarised as follows:

1. In normal exercise people with no respiratory history or disease, heavy exercise in 0.2 ppm or O3 causes a reduction in ventilatory flow rates after two hours of exposure. This response is usually accompanied by mild symptoms of respiratory irritation[27]; occurs similarly in smokers and nonsmokers; can be demonstrated in children[28]; may be slightly greater in women than in men[20]; and in one individual is highly reproducible on different occasions[27]. However, there are considerable differences in response between individuals[27].

2. The response is dependent on ventilation rate and on ozone concentration[11,26,32].

3. If exposures are given on consecutive days, the response diminishes after the second day. This 'adaptation' lasts for about ten days[19]. The mechanism of this effect is not yet fully understood.

4. There is evidence that ozone is stimulating an 'irritant receptor' system in the lung; the first effect of this is to limit an individual's ability to take a maximal deep breath[12].

This effect is not prevented by the administration of pharmacological compounds that relieve the airway constriction that occurs in asthma.

5. Asthmatic subjects are not specially sensitive to ozone[22,33], though they are much more sensitive to $SO_2$ and sulphates than is the non-asthmatic population[18,35].

6. Levels of ozone of 0.5 ppm or more cause a reduction in the maximal oxygen uptake possible during severe exercise[3,9].

Studies of normal children exercising at summer camps show that decrements in ventilatory tests can be shown to be occurring on days of higher ozone levels, even when these do not reach maxima of more than 0.12 ppm[17,24,25]. These studies confirm in the field, similar observations made under controlled conditions.

There are two other phenomena of importance that follow ozone exposure.

7. The general reactivity of the airway (as quantitated by the airflow limitation that follows inhalation of a known concentration of a physiological constrictor) increases after ozone expsoure, and remains

elevated for about a week[6,14].

8. Ozone increases the permeability of the lung; this accompanies the limitation of inspiration in normal subjects. Its significance is not yet understood.

There is of course much discussion as to how concerned we should be that these reversible effects are occurring at current ambient levels of this intensely irritating gas. I shall give an opinion on that question after reviewing the epidemiological data.

EPIDEMIOLOGICAL STUDIES

There are many reasons why epidemiological studies are difficult to plan and difficult to interpret[8]. In the case of ozone, the present data leads to the folowing conclusions:

1. There is evidence that ozone levels are related to aggravation of asthma attacks. This was first shown to be occurring in Los Angeles[36]; a more recent study in Houston, with more precise exposure measurement and much better characterization of the subjects, has confirmed that ozone levels are closely related to an increased risk of an attack in known asthmatics[13,34]. In this study, the histogram of ozone levels showed variation betwen 0.06 and 0.14 ppm of ozone during the study period (these are not high levels - they are slightly lower than those recorded every year in Southern Ontario, or that exist in many regions of the Northeast United States).

2. It is possible to show in a large population (5.8 million), that the elevated ozone and $SO_4$ levels during the summer months in Ontario are associated with an increased rate of hospital admission for acute

respiratory illness[4,5]. It is not possible to separate the effect of ozone from that of $SO_4$ since these are very closely correlated. It is possible that both are involved in the increased morbidity; or conceivably that neither are, but they act as surrogates for some other species that 'travel' with these two.

3. However, there do not appear to be major differences in respiratory symptoms between populations living in high oxidant regions and those in lower, within the Los Angeles basin[21]. Differences in cross-sectional studies of pulmonary function have not been large[3].

4. Correlative studies between ozone levels and recorded "reduced activity days" in the U.S. population suggest a relationship[30]; but specific interpretation of this kind of study is difficult.

5. Neither the acute chamber studies nor the present epidemiological data provide evidence of possible long-term adverse effects, either for ozone or for sulphates.

CONCLUSIONS

It is clear that ozone is an intensely irritant gas, capable of reducing ventilatory flow rate in normal subjects at concentrations to which large numbers of people are now intermittently exposed. It is not proven that ozone is related to the increased rate of hospital admissions for asthma that have been noted in different parts of the world; but it does appear to be the case that levels up to 0.16 ppm (and probably above 0.08 ppm) are consistently associated with increased hospital admissions for acute respiratory disease.

The question of whether transient changes in ventilatory flow rate "matter", can only be answered when we fully understand the mechanisms

of ozone action on the lung. Until we have evidence that repetitive ozone exposure is without long-term adverse and irreversible effects, and until we understand more fully the factors that lead to acute exacerbation of asthma (particularly the role of non-specific airway reactivity), we should take a serious view of the exposure of large numbers of people to concentrations above the present Canadian standard of 0.08 ppm for a one hour exposure. This 'conservative' view is supported by a large volume of animal exposure work that indicates that adverse morphological changes occur at concentrations in excess of 0.25 ppm, and that oxidants lower the animal's resistance to respiratory infections[7,10,29,33].

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DEUXIÈME SÉANCE/SESSION II

FORMATION DES OXYDANTS/OXIDANT FORMATION

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Service de l'environnement atmosphérique
Environnement Canada/Atmospheric Environment Service
Environment Canada

# CHEMISTRY OF OXIDANT FORMATION
# IMPLICATIONS FOR DESIGNING EFFECTIVE CONTROL STRATEGIES

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## RÉSUMÉ

Un simple modèle boîte, mobile, a servi à évaluer l'incidence de diverses stratégies d'atténuation sur les prévisions de la formation de l'ozone en milieux urbains. D'après ce modèle, l'efficacité des mesures de réduction envisagées dépend étroitement du rapport entre les précurseurs, les composés organiques volatils (COV) et les oxydes d'azote ($NO_x$) émis en milieux urbains. Selon les hypothèses énoncées sur le rapport entre les émissions de COV et de $NO_x$, une stratégie impliquant à la fois la réduction des COV et des $NO_x$ entraînerait une réduction plus ou moins grande des concentrations d'ozone sous le vent et serait de fait plus ou moins efficace qu'une stratégie faisant intervenir la réduction des COV seulement. En général la simple réduction des $NO_x$ a un effet négatif sur les concentrations d'ozone près des sources. D'ailleurs, quand la réduction des $NO_x$ accompagne celle des COV, les concentrations d'ozone près des sources sont plus fortes qu'avec la réduction des COV uniquement. Aussi, il semble que l'exposition de la population à des concentrations accrues d'ozone augmente avec la réduction des $NO_x$ contrairement à celle des COV.

# CHEMISTRY OF OXIDANT FORMATION

## IMPLICATIONS FOR DESIGNING EFFECTIVE CONTROL STRATEGIES

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## ABSTRACT

A simple moving box model was used to assess the effect of various control strategies on predictions of ozone formation in urban areas. It was found that the effectiveness of a proposed control measure depends critically on the ratio of the Volatile Organic Compounds (VOC) and $NO_x$ precursors that are emitted into the urban environment. Depending on the assumptions made about the ratio of the VOC and $NO_x$ emissions, a strategy involving simultaneous control of VOC and $NO_x$ can be more or less effective in reducing downwind ozone levels than a strategy involving reduction of only VOC. In all cases, however, it was found that $NO_x$ control, by itself, has a detrimental impact on ozone levels near source areas. Further, when $NO_x$ control accompanies VOC control, ozone concentrations near source areas are higher than would occur if VOC alone is reduced. $NO_x$ control, therefore, could result in greater population exposure to high ozone levels than would be the case if only VOC is reduced.

## INTRODUCTION

The control of Volatile Organic Compounds (VOC) has been the principal approach used in recent years to reduce ambient concentrations of ozone in urban areas. Several recent reviews on control strategies for ozone (CARR, 1986; Meyer, 1986), however, have suggested that there may be situations where control of $NO_x$ emissions could also be beneficial in reducing urban ozone levels. The present study was undertaken in an effort to determine if $NO_x$ control, either alone or in combination with VOC control, could be effective in reducing ozone levels in urban areas.

The effectiveness of any measure that might be adopted to limit ozone formation is largely determined by the ratio of the VOC and $NO_x$ precursors that are emitted into the environment. The fact that this is the case is apparent if one understands the chemical processes that are responsible for the production of ozone. In the following section, a discussion of the chemistry of oxidant formation and the relationship between emission control measures and $VOC/NO_x$ ratios is presented. The results of simulations conducted with a simple box model to investigate emission control strategies are also presented and the implication of these results on the possible benefits to be achieved through $NO_x$ control is discussed.

## CHEMISTRY OF OXIDANT FORMATION

Ozone formation in the atmosphere is governed by three reactions. Nitrogen dioxide photolyses in sunlight to produce nitric oxide and an oxygen atom:

$$NO_2 + h\nu \rightarrow NO + O \qquad (1)$$

The O atom liberated reacts rapidly with oxygen in the presence of a third body to generate ozone:

$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$

In the absence of any competing reactions, the ozone produced in Reaction (2) reacts with NO to regenerate $NO_2$:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (3)$$

As a result of these three reactions, an equilibrium or steady-state condition is established and the concentration of ozone is given by the Steady-State Equation,

$$[O_3] = k_1 \times ([NO_2]/[NO]) \times \text{Constant},$$

where $k_1$ is the rate of photolysis of $NO_2$. Most of the $NO_x$ emitted into the urban environment is in the form of NO. In fact, the ratio of $NO_2$-to-NO emissions from combustion sources is approximately 1-to-9 (U.S. EPA, 1982). Given such a low ratio, it is apparent from the Steady-State Equation that there will be little build-up of ozone in the atmosphere unless there is a mechanism for converting NO to $NO_2$. Reactions (1) - (3) do not provide such a mechanism since every time an $O_3$ molecule is formed, it is immediately consumed through reaction with NO. An alternate pathway is needed that will lead to the oxidation of NO without destroying $O_3$ in the process. Such a pathway is provided through the oxidation of VOC's.

VOC's participate in a number of reactions that increase the $NO_2$-to-NO ratio and consequently increase the levels of $O_3$ observed in the atmosphere. For example, aldehydes, which are components of auto exhaust, photodissociate in sunlight to produce $HO_2$ radicals that rapidly oxidize NO:

$$RCHO + h\nu \rightarrow HO_2 \quad (4)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (5)$$

The hydroxyl radicals liberated in this process react readily with most hydrocarbon species to produce alkylperoxy radicals which also oxidize NO:

$$OH + HC \rightarrow RO_2 \quad (6)$$

$$RO_2 + NO \rightarrow RO + NO_2 \quad (7)$$

The resulting RO radicals react readily with oxygen:

$$RO + O_2 \rightarrow RCHO + HO_2 \quad (8)$$

The aldehydes formed in this process can either photodissociate to start the process over again or they can react with OH radicals:

$$RCHO + OH \rightarrow RCO_3 \quad (9)$$

The acylperoxy radicals formed in this process can also oxidize NO:

$$RCO_3 + NO \rightarrow RO_2 + NO_2 \quad (10)$$

In addition to Reactions (4) - (10), which increase the $NO_2/NO$ ratio and promote $O_3$ formation, there are also reactions that tend to decrease the $NO_2/NO$ ratio and limit $O_3$ production. The two most important of these processes are the reactions of OH and $RCO_3$ radicals with $NO_2$ to form nitric acid and peroxyacetylnitrate, respectively:

$$OH + NO_2 \rightarrow HNO_3 \quad (11)$$

$$RCO_3 + NO_2 \rightarrow PAN \quad (12)$$

The significance of these reactions will become apparent later.

The rate of conversion of NO to $NO_2$ in the atmosphere is governed largely by the VOC-to-$NO_x$ ratio. At low ratios ($VOC/NO_x$ < 5:1), the system is VOC-limited and $NO_x$-rich. Few $RO_2$ radicals are produced as a result of hydrocarbon oxidation (Reaction 6) and the rate of conversion of NO to $NO_2$ is slow. The VOC's may be depleted before all of the NO has been oxidized to $NO_2$, in which case the build-up of ozone will be limited. An effective control strategy in such a situation would be to reduce the limiting reactant which is VOC. Such a strategy would have the effect of further decreasing the number of $RO_2$ radicals available to oxidize NO and ozone levels would decrease.

At high $VOC/NO_x$ ratios ($VOC/NO_x$ > 20:1), the system is VOC-rich and $NO_x$-limited. The radicals produced during oxidation of the VOC's are in excess of the number needed to oxidize NO. The excess radicals consume $NO_2$ through Reactions (11) and (12) and limit $O_3$ production. An effective control strategy in such a situation would be to reduce the limiting reactant which in this case is $NO_x$. Fewer of the excess radicals would then be consumed through reaction with NO. More of the radicals would be available to react with $NO_2$ to remove it from the system and retard $O_3$ formation.

At moderate VOC-to-$NO_x$ ratios, both VOC and $NO_x$ are present in the amounts needed to generate ozone effectively. The VOC's produce sufficient $RO_2$ radicals to oxidize all NO to $NO_2$. $NO_x$ levels are also sufficient to generate high levels of $NO_2$. In such a situation, control of either VOC or $NO_x$ should lead to reduced ozone levels.

The role of the $VOC/NO_x$ ratio in determining the effectiveness of various control measures can be better illustrated through the use of an ozone isopleth diagram. Such a diagram is illustrated in Figure 1. In this diagram, maximum daily ozone concentrations are plotted as a function of early morning levels of $NO_x$ and non-methane

hydrocarbons (NMHC).* These isopleths were generated with a very simple moving box model, which is the basis of the Empirical Kinetics Modeling Approach (EKMA) that is used to estimate the amount of precursor control needed to reduce peak hourly ozone levels (U.S. EPA, 1977). Regardless of the model used to generate the diagram, whether it is a simple box model or a sophisticated dispersion model, the shape of the diagram will be similar. All such diagrams show three distinct regions. In the upper left-hand corner of the diagram, the isopleth lines are parallel and have a positive slope. There is a region in the middle of the diagram where the isopleths exhibit considerable curvature and finally, in the lower right-hand corner, the isopleth lines are all parallel to the x-axis.

The isopleth diagram can be used to understand the relationship between emission control measures and $VOC/NO_x$ ratios. Figure 1 demonstrates the effect of reducing ozone precursor concentrations by 25% in the low $VOC/NO_x$ regime of the diagram where VOC's are the limiting reactant in the $O_3$-formation process. Point A corresponds to a $VOC/NO_x$ ratio of 3:1 and a maximum ozone concentration of 0.24 ppm. Reducing VOC concentrations by 25% will decrease peak ozone to 0.12 ppm (Point B). Since the curves have a positive slope, however, a 25% decrease in $NO_x$ will lead to an increase in ozone concentration as can be seen by Point C which corresponds to an ozone level of 0.29 ppm. To achieve the same benefit that is obtained through a 25% reduction in VOC, $NO_x$ concentrations would have to be reduced by 95% (Point D).

Figure 2 demonstrates the effect of reducing ozone precursors in the high $VOC/NO_x$ regime of the diagram where VOC's are in excess of the amount needed to generate $O_3$ effectively. Starting at Point A, which corresponds to a $VOC/NO_x$ ratio of 30:1, a 25% reduction in $NO_x$

*In this paper, VOC and NMHC will be used interchangeably. Usually, however, NMHC is used to denote ambient concentrations while VOC is used to denote emissions of organic compounds.

will decrease ozone levels by approximately 15% (Point B). Because the ozone isopleths are parallel to the x-axis, however, a 25% reduction in VOC will cause no change in predicted ozone levels (Point C). To achieve the same benefit in $O_3$ that is achieved through a 25% reduction in $NO_x$, VOC levels would have to be reduced by 70% (Point D.)

The effect of reducing $O_3$ precursors at intermediate ratios is shown in Figure 3. It is in this region of the diagram where control of either VOC or $NO_x$ should lead to reduced $O_3$ levels. In general, this region encompasses VOC/$NO_x$ ratios between about 5:1 and 20:1. Most urban areas fall within this region. In a recent analysis of VOC and $NO_x$ measurements conducted in 29 cities, it was found that 25 of the cities had median VOC/$NO_x$ ratios that fell between 8 and 15 with an overall median value of about 12:1 (Baugues, 1986). Starting at Point A in Figure 3, which corresponds to a VOC/$NO_x$ ratio of 12:1, it can be seen that a 25% reduction in either VOC or $NO_x$ concentrations is equally effective. Control of either will reduce ozone from 0.28 to 0.25 ppm. If both VOC and $NO_x$ are controlled by 25% (Point D), peak ozone concentrations would be reduced even further to about 0.23 ppm.

Judging from the example shown in Figure 3, it appears that control of either VOC or $NO_x$ might be equally effective and control of both precursors might be the most effective strategy of all for urban areas having typical VOC/$NO_x$ ratios. In the example shown in Figure 3, however, the control measures implemented were not sufficient to reduce $O_3$ to the U. S. National Ambient Air Quality Standard of 0.12 ppm. The amount of reduction that would be needed to achieve the $O_3$ standard for this particular case is shown in Figure 4. As is evident from this figure, the most effective strategy for achieving the $O_3$ standard would be to control VOC. The majority of the modeling studies conducted to date do suggest that a pure VOC control strategy is the most effective one for achieving the ozone standard. Many of these studies, however, suggest that some other type of control strategy might be more

effective in the short term for achieving more immediate benefits. Figure 5 presents the results of one such study that was conducted by Meyer (1986). Meyer first constructed an isopleth diagram using certain assumptions regarding the reactivity of the urban VOC mix, emission patterns, dilution, etc. The isopleth diagram was then used to look at the effect of various control scenarios on daily maximum $O_3$ levels. In this example, the VOC/$NO_x$ ratio and the daily maximum ozone were assumed to be 12:1 and 0.24 ppm, respectively. Figure 5 shows the decrease in ozone that would be achieved through control strategies involving relative reductions in VOC, $NO_x$ or both VOC and $NO_x$. It is evident from this figure that, for moderate reductions in ozone precursors, the least effective strategy would be control of VOC alone. For example, a 30% reduction in $NO_x$ would be more effective than a 30% reduction in VOC and the most effective strategy would be to control both by 30%. The curves, however, eventually cross and the most effective strategy for achieving the ozone standard would be to control only VOC.

The results presented in Figures 3 and 5 suggest that, if we are looking for early reductions in ozone and maximum short-term benefits, the most effective strategy might be to adopt a control measure that involves reduction of both VOC and $NO_x$. These figures, however, only demonstrate the potential benefit of emission reductions on the daily maximum ozone level, regardless of where that maximum occurs. The figures do not indicate how ozone levels throughout an urban area might be impacted by emission reductions. In order to investigate the effect of VOC and/or $NO_x$ reductions on area-wide ozone levels, a series of simulations were carried out using a simple model. The results of these simulations are presented in the following sections.

## SIMULATION CONDITIONS

A simple one-cell moving box model was used to assess the effect of VOC and $NO_x$ control strategies. For the baseline condition, the VOC and $NO_x$ concentrations in the box at the start of the simulation were assumed to be 1.0 ppmC and 0.1 ppm, respectively, for an initial VOC/$NO_x$ ratio of 10:1. The initial concentration of $NO_2$ was assumed to be 25% of the initial $NO_x$. Simulations were carried out from 0800 to 1800 hours using a solar radiation profile that corresponded to summer solstice at 34° latitude. Emissions were added to the box as it moved along its trajectory. It was assumed that the VOC/$NO_x$ ratio of the added emissions was also 10:1, the same as the ratio of the initial mix. Emissions equivalent to 70% of the initial VOC and $NO_x$ concentrations were added over an 8-hour period, with the largest fraction of the added emissions occurring during the first several hours of the simulation. The mixing height was allowed to vary from 250 m to 1235 m. As the mixing height rose, ozone and aged VOC's from aloft were entrained into the box. The concentrations of the entrained ozone and VOC pollutants were 0.05 ppm and 0.025 ppmC, respectively. The composition of the surface-layer VOC's was based on a recent analysis of VOC measurements that were conducted between 0600 and 0900 hours in 22 cities over a two-year period (Baugues, 1986). The composition of the VOC's entrained from aloft was based on an analysis of aircraft VOC measurements that were conducted over four different cities (Baugues, 1987). The chemical mechanism used in the simulations was the Carbon-Bond IV Mechanism that was recently developed by Whitten and Gery (1986). The CBM-IV contains 70 reactions and 28 species; VOC's are partitioned among seven organic classes. The mechanism has been extensively tested against smog chamber data collected in several different chamber facilities.

Simulations were conducted using a computer program developed by Jeffries (1987). The program is designed to run on an IBM PC/XT/AT

or fully compatible computer. The software package contains many of the same options that are available in the OZIPM-2 computer program (Gipson, 1984a) that is designed for use on mainframe computer systems.

## SIMULATION RESULTS

The $O_3$ profile generated for the baseline condition ($[VOC]_i$ = 1.0 ppmC, $[NO_x]_i$ = 0.1 ppm) is shown in Figure 6. Also shown is the effect of reducing the initial VOC concentration and the added VOC emissions by 50%. The x-axis in this figure can be viewed as distance downwind from the source area as well as time. What is evident from the profiles shown in this figure is that VOC control leads to reduced ozone levels at all points along the trajectory. As a consequence, ozone levels throughout the urban area as well as downwind ozone levels are expected to be lowered if a VOC control strategy is adopted. This is not the case, however, if the initial $NO_x$ and the $NO_x$ emissions are decreased by 50%. As shown in Figure 6, reduction in $NO_x$ leads to an increase in ozone levels in the early stages of the simulation when source emissions are greatest. Since more people tend to live in the center of urban areas than in downwind locations, $NO_x$ control could result in increased population exposure to ozone.

A comparison of the $NO_x$ and VOC control profiles shown in Figure 6 indicates that, along most of the trajectory, ozone levels following $NO_x$ control are considerably higher than $O_3$ levels following VOC control, in some cases by as much as a factor of three. The curves, however, do come together in the late stages of the simulation, and the maximum ozone level obtained following $NO_x$ control is comparable to the maximum ozone obtained following VOC control (0.185 vs. 0.190 ppm).

The effect of reducing both VOC and $NO_x$ by 50% is shown in Figure 7. During the first half of the simulation, ozone levels are

higher when both precursors are controlled than when only VOC is controlled. Downwind ozone levels, however, are substantially lower for the case where both VOC and $NO_x$ are controlled (0.16 vs. 0.19 ppm). Combined VOC and $NO_x$ control, therefore, does reduce peak ozone; consequently, downwind ozone levels should be reduced if such a control strategy were adopted.

Judging from the results presented in Figure 7, it appears that a strategy involving simultaneous control of VOC and $NO_x$ might be more effective than a strategy involving reduction of only VOC. There is one important point that should be noted, however. The simulations presented in Figures 6 and 7 were conducted assuming that the VOC/$NO_x$ ratio of the emissions was the same as the ratio of the pollutants present in the box at the start of the simulations. For the baseline simulation, this led to a VOC/$NO_x$ emission ratio of 10:1. This ratio was selected because urban VOC and $NO_x$ measurements indicate that the ambient ratio is at least as high as 10:1 in most urban areas (Baugues, 1986). Existing emission inventories, however, suggest that ambient VOC/$NO_x$ ratios should be considerably lower than 10:1. Recent reviews of emission inventories indicate that there may be a factor of two discrepancy between VOC/$NO_x$ ratios based on emission inventories and those derived from ambient measurements (Ching et al., 1986, Westberg and Lamb, 1985). To judge the effect of this uncertainty in emission estimates, the simulations presented in Figures 6 and 7 were repeated using an emissions profile derived from an analysis of the St. Louis RAPS emission inventory (Gipson, 1984b). This profile resulted in a VOC/$NO_x$ emission ratio of 5:1 in contrast to the 10:1 ratio that was used for the baseline simulation shown in Figures 6 and 7.

The results obtained when the ratio of the VOC/$NO_x$ emissions was reduced to 5:1 are shown in Figures 8 and 9. As in the earlier set of simulations, the VOC/$NO_x$ ratio of the initial mix was still assumed to be 10:1 for the baseline simulation; only the ratio of the added

emissions was changed. A comparison of the effect of $NO_x$ control vs. VOC control is shown in Figure 8. If this figure is compared with Figure 6, it is apparent that the increase in ozone that occurs during the early stages of the simulation when $NO_x$ is reduced is more pronounced when the ratio of VOC/$NO_x$ emissions is 5:1 than when it was 10:1. In addition, although the previous set of simulations showed peak downwind ozone levels that were comparable when either $NO_x$ or VOC was reduced, the simulations presented in Figure 8 show that VOC control is clearly more effective than $NO_x$ control in reducing peak ozone as well as ozone all along the trajectory. The maximum $O_3$ concentration after VOC control is 0.15 ppm in contrast to the 0.22 ppm that is obtained following $NO_x$ control.

The ozone profile generated when both VOC and $NO_x$ are reduced by 50% is shown in Figure 9 for the case with the lower VOC/$NO_x$ emission ratio. If this profile is contrasted with the profile obtained when only VOC is reduced, it is apparent that control of $NO_x$ in addition to VOC is counterproductive. This is in contrast to the results presented in Figure 7 which suggested that a combination of VOC and $NO_x$ controls would be the most effective strategy for reducing downwind levels of ozone.

## DISCUSSION

The ozone profiles presented in Figures 7 and 9 suggest that control of both VOC and $NO_x$ could be more or less effective than control of VOC alone depending on the assumptions made regarding the ratio of the precursors that participate in the ozone-forming process. Comparable results have been obtained in modeling studies that have been conducted with sophisticated photochemical grid models. In a study sponsored by the California Air Resources Board (SCAQMD, 1981), the urban airshed model developed by Systems Applications, Inc. was used to investigate the effect of emission reductions in the South

Coast Air Basin. In that study, the model was exercised for a one-day period beginning at 0500 hours. The model was initialized using surface air monitoring data for VOC and $NO_x$. Initial concentrations in the aloft layers were assumed to be equal to the concentrations in the ground-level cells of the model. As a consequence of using ambient data to initialize the model, the initial concentrations of VOC and the resulting $VOC/NO_x$ ratios were high in comparison to the values that would be derived from the emission inventory. The simulations, therefore, were driven by the initial conditions and not by the emission inventory.

Using the scenario described above, the model developers looked at the effect of reducing either VOC or both VOC and $NO_x$ by 50%. They found that VOC control alone was less effective in reducing the daily maximum $O_3$ concentration than control of both VOC and $NO_x$. A 50% reduction in VOC led to a 19% decrease in the area-wide predicted ozone maximum whereas a 50% decrease in both VOC and $NO_x$ reduced the basinwide predicted maximum by 26%. They found, however, that ozone concentrations near the source areas were higher when both VOC and $NO_x$ were reduced than when only VOC was reduced. These results are in qualitative agreement with the results presented in Figure 7.

In a subsequent study ( Tesche et al., 1984), the model developers again exercised their urban airshed model to look at the effect of emission reductions in the South Coast Air Basin. In this later study, however, the model was exercised for a two-day period so that the results on the second day would be governed primarily by the emissions and not by the air quality data used to initialize the simulation. Thus, in contrast to the earlier work, the simulations conducted in this later study were driven by the low $VOC/NO_x$ ratio of the emission inventory as opposed to the much higher $VOC/NO_x$ ratio of the ambient measurements. In this study, as in the previous one, the model developers used an emission inventory compiled in 1974 which,

when converted from a mass basis to a volume basis, suggested a spatially-averaged VOC/$NO_x$ ratio of 4.7. This is comparable to the VOC/$NO_x$ emission ratio of 5:1 that was used to generate the basecase ozone profile shown in Figure 9.

Using the emission-driven scenario, Tesche et al. (1984) compared the effect of reducing VOC emissions by 50% versus the effect of reducing both VOC and $NO_x$ emissions by 50%. They found that reductions in VOC alone led to a 25% decrease in the basinwide $O_3$ maximum. When both VOC and $NO_x$ were reduced, the basinwide $O_3$ maximum was decreased by only 20%. In contrast to the earlier study, Tesche et al. concluded that $NO_x$ control accompanied by VOC control is less effective than control of VOC emissions alone. This finding is in agreement with the results presented in Figure 9.

Both the box model used in this study and the urban airshed modeling results suggest that control of both VOC and $NO_x$ could be more effective in lowering daily maximum $O_3$ levels than control of VOC alone if the simulations are governed by VOC/$NO_x$ ratios derived from ambient measurements. The reverse appears to be true if the simulations are driven by ozone-precursor ratios that are derived from emission inventories.

## CONCLUSIONS

The results presented in this paper, as well as the results obtained in other modeling studies, leave little doubt that VOC reduction is the most effective strategy for reducing ozone levels in urban areas having VOC/$NO_x$ ratios of 10 or less. At VOC/$NO_x$ ratios of 20 or more, $NO_x$ reduction is clearly the most effective strategy for reducing ozone. At intermediate ratios between approximately 10:1 and 20:1, control of either VOC or $NO_x$ could be an effective strategy for reducing ozone levels. Which one will be the most effective will

depend on a number of factors. For urban areas having typical VOC/$NO_x$ ratios (<15:1), VOC control will probably be the most effective strategy for achieving the ozone standard. At higher ratios (>15:1), $NO_x$ reduction may be more effective for achieving the ozone standard. The results obtained in this study, however, suggest that $NO_x$ control can lead to an increase in ozone levels near source areas; consequently, a greater fraction of the population may be exposed to high ozone levels if such a strategy is adopted.

The profiles presented in Figures 6-9 demonstrate that the critical factor in determining the most effective control measure for reducing urban $O_3$ levels is the VOC/$NO_x$ ratio. Depending on the assumptions made regarding the ratio of the $O_3$-precursor emissions, a strategy involving simultaneous reduction of VOC and $NO_x$ may be more or less effective in reducing downwind ozone levels than a strategy involving reduction of only VOC. Given the present uncertainty in emission inventories, it is difficult to assess which control strategy would be the most effective.

In order to judge the effectiveness of simultaneous VOC and $NO_x$ control, the accuracy of existing emission data bases needs to be determined. A more complete and accurate data base of ambient VOC/$NO_x$ ratios in urban areas also should be acquired. Until emissions and ambient measurements are reconciled, we should be very cautious about embarking on any control program that involves reductions in $NO_x$. Such a strategy could have a detrimental impact on urban ozone levels.

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FIGURE 1

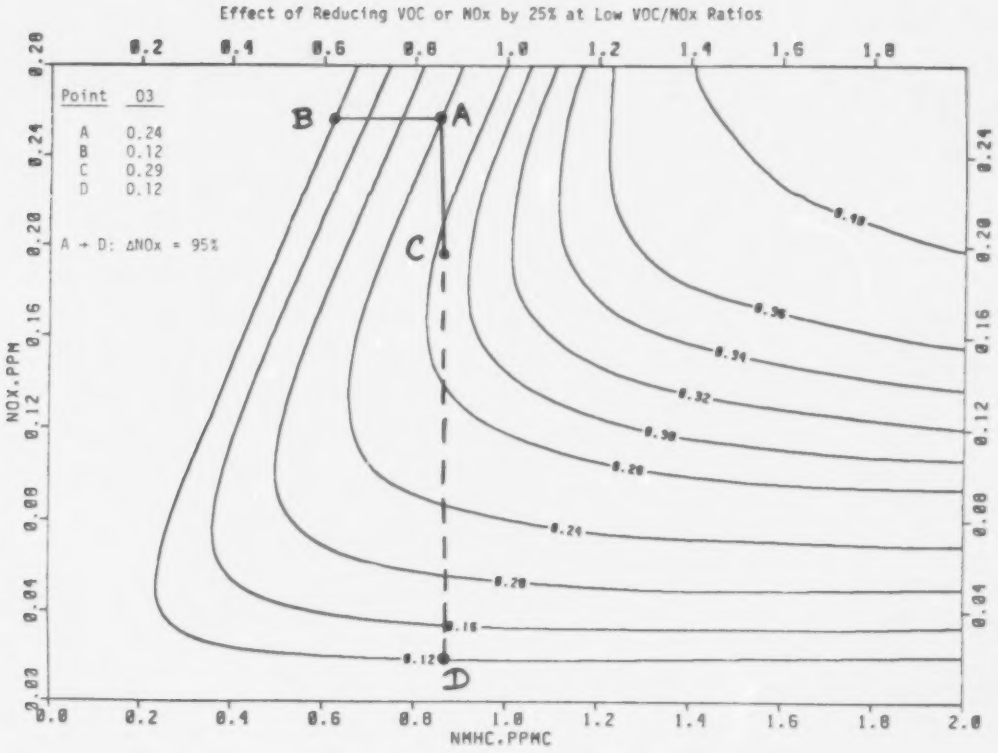



FIGURE 2

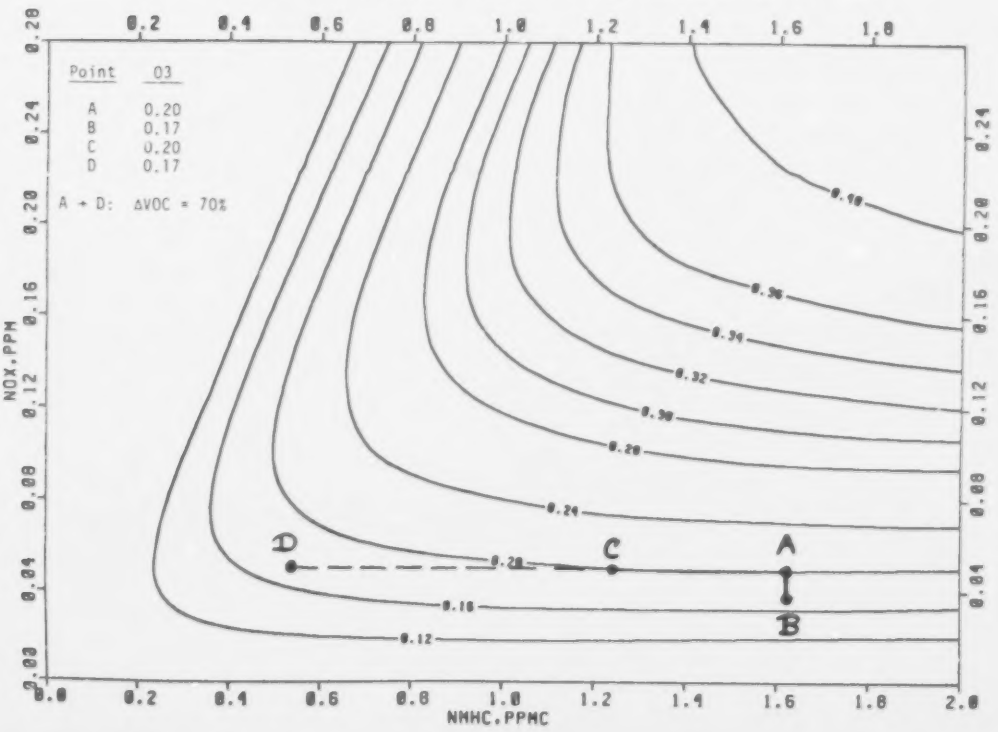


FIGURE 3

Effect of Reducing VOC and NOx by 25% at Intermediate VOC/NOx Ratios

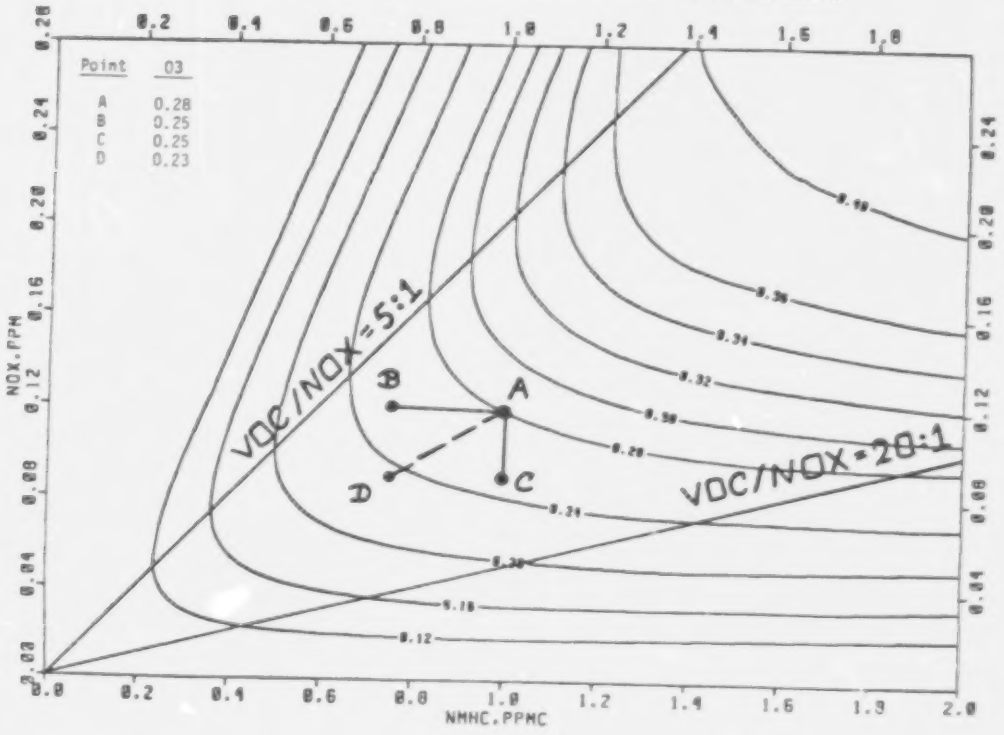



FIGURE 4

Control Measures Needed to Achieve Ozone Standard at VOC/NOx = 12:1

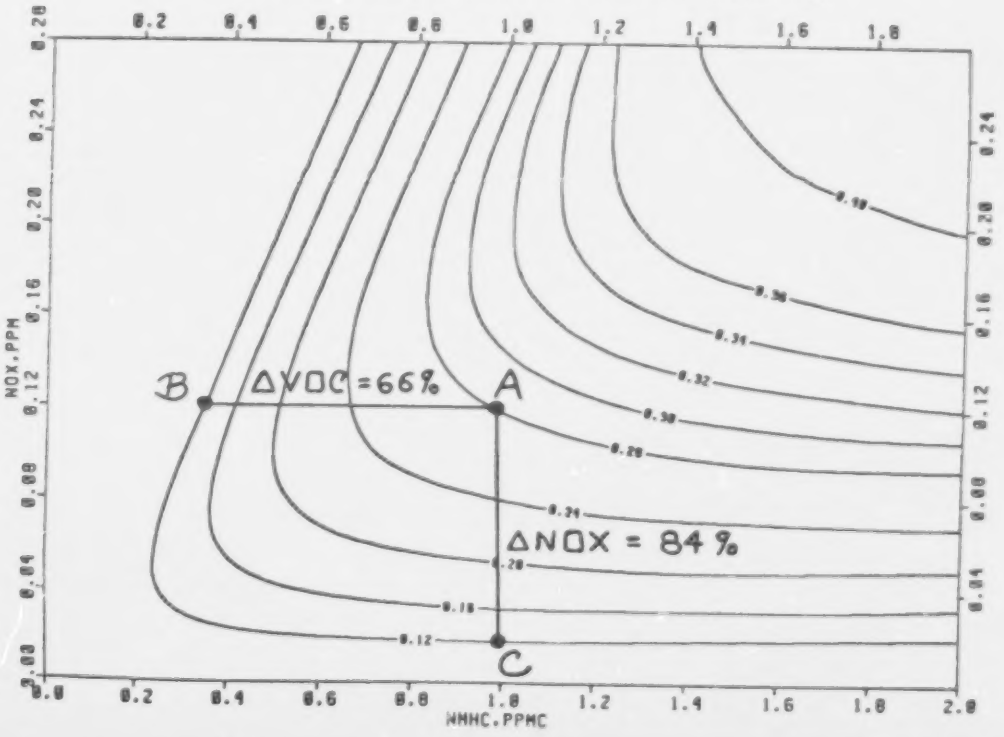
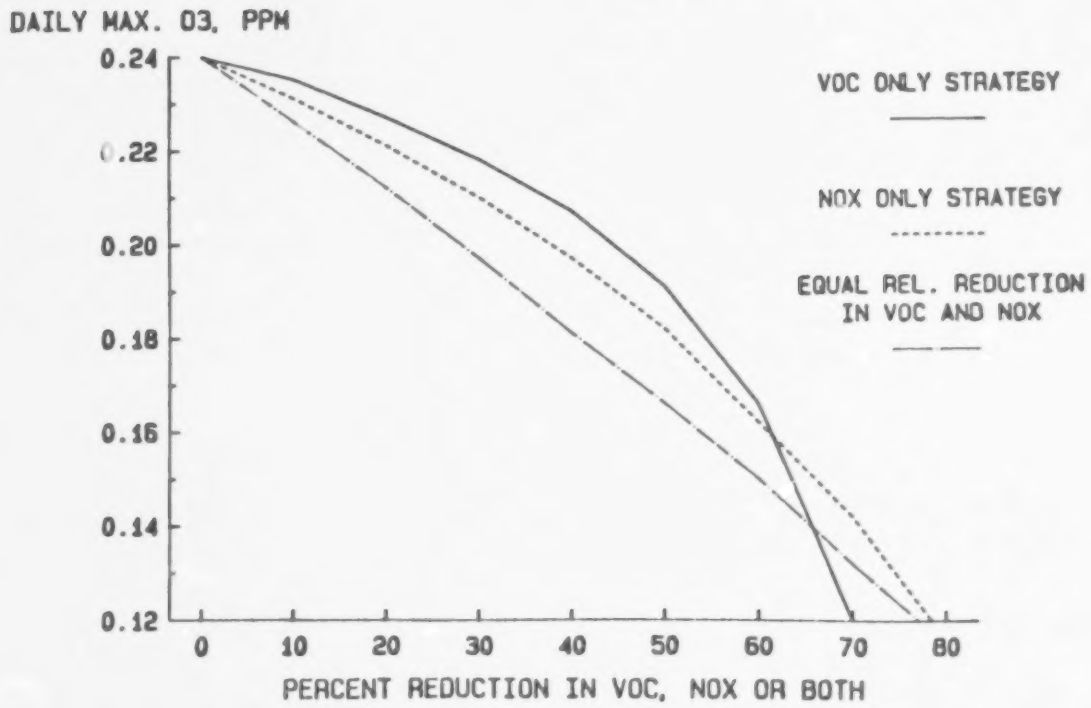


FIGURE 5

## DAILY MAXIMUM OZONE AS A FUNCTION OF APPLIED CONTROLS



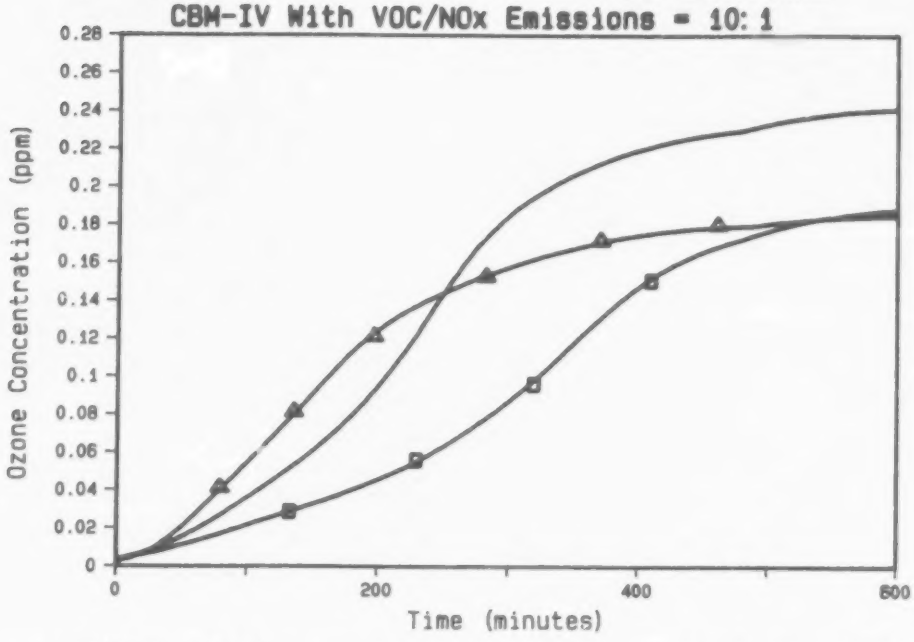

VOC/NOX RATIO = 12:1

SOURCE: MEYER (1986)

# FIGURE 6

## COMPARISON OF VOC VS. NOX CONTROL

**CBM-IV With VOC/NOx Emissions = 10: 1**

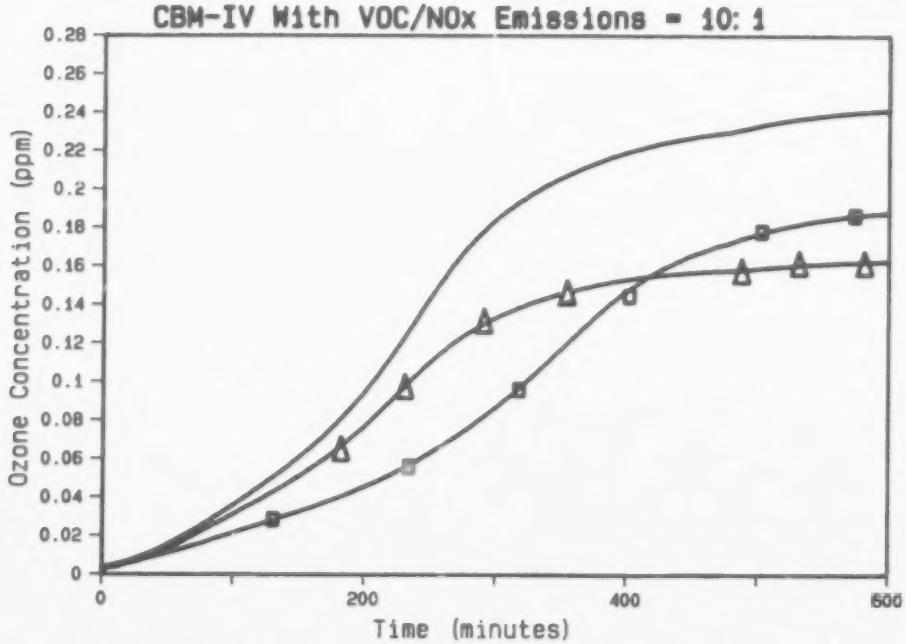



— VOC=1, NOX=0.1 □ VOC=0.5, NOX=0.1 △ VOC=1, NOX=0.05

# FIGURE 7

## COMPARISON OF VOC VS. VOC + NOX CONTROL

**CBM-IV With VOC/NOx Emissions = 10: 1**

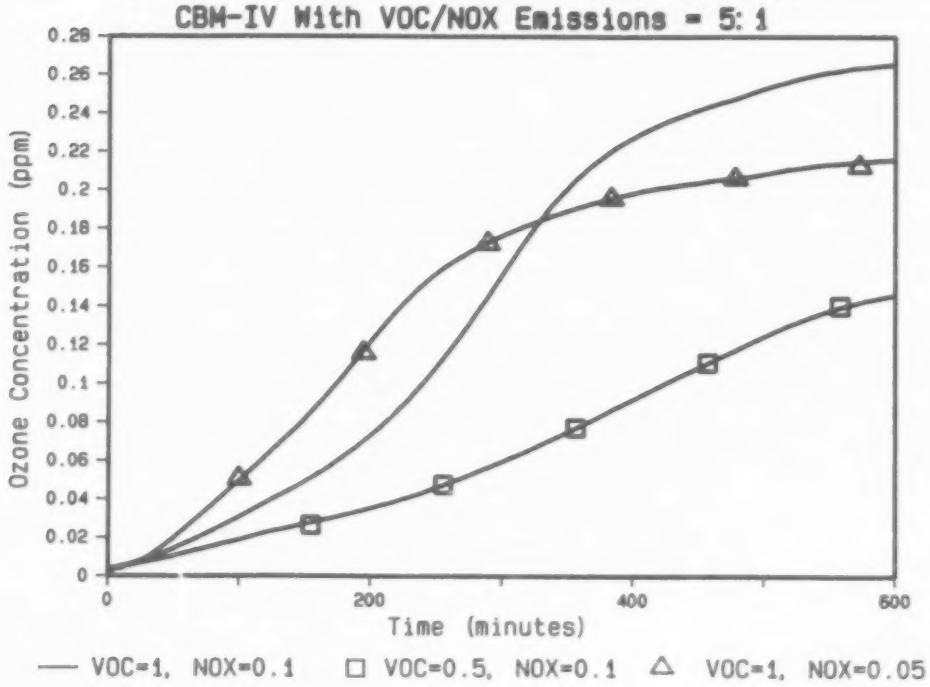



— VOC=1, NOX=0.1 □ VOC=0.5, NOX=0.1 △ VOC=0.5, NOX=.05

# FIGURE 8

## COMPARISON OF VOC VS. NOX CONTROL

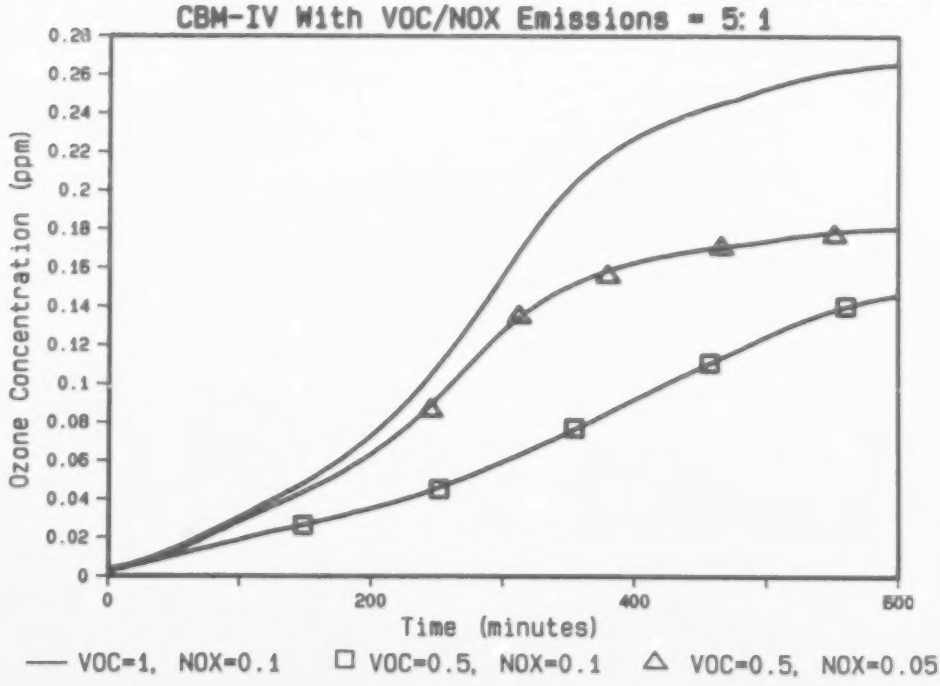
### CBM-IV With VOC/NOX Emissions = 5: 1




# FIGURE 9

## COMPARISON OF VOC VS. VOC + NOX CONTROL

### CBM-IV With VOC/NOX Emissions = 5: 1



# EVALUATION OF A SURROGATE SPECIES CHEMICAL REACTION MECHANISM

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## RÉSUMÉ

L'un des éléments critiques des modèles sur la qualité de l'air utilisés pour élaborer des stratégies d'atténuation des oxydants est le mécanisme chimique atmosphérique. Le présent exposé décrit donc les méthodes et les résultats d'une étude visant à évaluer un mécanisme chimique récemment révisé en fonction des données recueillies en laboratoire. Ce mécanisme chimique permet de retracer la formation de l'ozone et autres oxydants dans des mélanges d'oxydes d'azote et de composés organiques autres que le méthane en présence d'air. Le mécanisme étudié est un mécanisme détaillé par lequel diverses espèces organiques individuelles sont traitées explicitement. Son évaluation s'est effectuée à partir de 491 expériences menées dans les chambres de simulation de quatre laboratoires différents. Les résultats de l'évaluation montrent que, dans la vaste majorité des cas, le mécanisme prédit les concentrations maximales d'ozone avec une erreur de $\pm$ 30 pour cent.

## ABSTRACT

A critically important component of the air quality models used to formulate oxidant control strategies is the atmospheric chemical mechanism. This paper describes the methods and results of a study to evaluate a recently updated chemical mechanism against environmental chamber data. The chemical mechanism describes the formation of ozone and other oxidants in mixtures of nonmethane organic compounds and nitrogen oxides in the presence of air. The mechanism tested in the study is a detailed mechanism in which many individual organic species are treated explicitly. The mechanism evaluation involved testing against 491 environmental chamber experiments conducted in four different chamber facilities. The results of the testing show the mechanism is able to predict the maximum ozone concentrations within ±30% in the vast majority of experiments.

## Introduction

The chemical reaction mechanism that describes the formation of ozone from nitrogen oxides ($NO_x$) and nonmethane organic compounds (NMOC) is a critically important component of the air quality models used to formulate oxidant control strategies. Until recently, the environmental chamber data base for the species involved in photochemical smog formation was too limited to comprehensively evaluate the atmospheric chemical reaction mechanisms. With the archiving of several major chamber data sets in the last few years (e.g., Carter et al. 1984; Jeffries et al. 1985), it is now possible to perform fairly rigorous evaluations of the performance of the chemical mechanisms for many individual organic compounds and mixtures of organic compounds.

This paper describes the methods and results of a study to evaluate an updated chemical reaction mechanism using environmental chamber data. Testing against environmental chamber data is the best currently available method of evaluating the mechanisms because of the controlled conditions and generally high-quality measurements in these experiments. Data from four environmental chambers were employed in the evaluation in order to obtain a broad range of initial reactant species and concentrations, and solar radiation intensities and spectral distributions. The overall objective of the study was to assess the accuracy of the updated mechanism under simulated atmospheric conditions.

## The Chemical Mechanism

The chemical mechanism employed in the evaluation is an updated and expanded version of the Atkinson et al. (1982) mechanism. The Atkinson et al. mechanism was updated for use in long-range transport modeling by Lurmann et al. (1986) and for urban-scale modeling by Carter et al. (1986) and Lurmann et al. (1987). The updated version, shown in

Table I, incorporates the kinetic and mechanistic data recommended by Atkinson and Lloyd (1984), NASA (1985), and Atkinson (1986). In addition, it incorporates updated reactions for ketones (acetone and methylethylketone), a new parameterized treatment of the aromatic ring-opening products from benzene, toluene, m-xylene, o-xylene, and mesitylene, and a generalized procedure for treating the radical-radical reactions involving alkyl peroxy and acyl peroxy radicals.

The chemical mechanism was expanded for the testing program to explicitly represent all of the organic compounds used as initial reactants in the single organic compound - $NO_x$ chamber experiments. The reactions for individual alkanes were based on the generalized alkane oxidation model of Carter and Atkinson (1985). For convenience, only the generalized reactions for lumped C4-C5 alkanes and greater than C6 alkanes are shown in Table I. The lumped C4-C5 alkane reaction parameters shown are for a mixture with equal mole fractions of n-butane, isobutane, n-pentane, and isopentane. The lumped C6+ alkane reaction parameters are based on equal weighting of the kinetic and product data for n-hexane, n-heptane, n-octane, 2,3-dimethylbutane, 2-methylpentane, 2,3-dimethylpentane, and iso-octane. The lumped alkane reactions are used instead of the reactions for individual alkanes when testing the mechanism against complex organic mixtures (and in atmospheric applications).

This chemical mechanism is a relatively detailed mechanism, yet there are still many organic compounds found in ambient air that are not explicitly included in the mechanism. In applying this mechanism to atmospheric problems, the surrogate species approximation in employed. With this approximation, the chemistry of the species in the mechanism which is most similar to the actual species is used as a surrogate for the actual species' chemical reactions. Without this approximation or comparable lumping approximations such as the carbon-bond method (Whitten et al. 1983), it would be impossible to simulate the reactions

of all the organic compounds found in ambient air. The mechanism used in this study has sufficient species to adequately describe the chemistry of the vast majority of organic species found in ambient air.

Chamber Characterization

In order to simulate environmental chamber experiments with a chemical mechanism, the environmental conditions in the chamber and processes occurring on the walls of the chamber must be characterized. The light intensity and spectral distribution are critical inputs since solar radiation is the driving force behind the ozone formation. For indoor chambers, the intensities and spectral distributions are constant or vary slowly in time so this is not a major uncertainty. However, this is a significant uncertainty in modeling outdoor experiments because both the intensity and spectral distribution are time-varying and are affected by sky conditions and the transmission properties of the Teflon walls.

It has been recognized for several years that the overall rates of oxidation in environmental chambers are higher than can be accounted for by known homogeneous processes (Carter et al. 1981; 1982). Heterogeneous wall reactions leading to formation of the hydroxyl radicals (OH) are suspected of being the principal source of this excess reactivity. For example, $NO_2$ and water vapor react on chamber walls to form nitrous acid which in turn photolyzes rapidly to form OH and NO. However, the measured rates of $NO_2$ hydrolysis [Sakamaki et al (1983) and Pitts et al (1984)] are to low to fully account for the indirectly measured OH radical flux from chamber walls (Carter et al. 1981, 1982). For this mechanism testing program, the chamber radical source strength were determined from radical tracer $NO_x$-air experiments carried out for the University of California, Riverside (UCR) chambers and from modeling $NO_x$-air and $NO_x$-butane runs for the University of North Carolina (UNC) chamber. This chamber effect is particularly important for modeling

slowly reacting organic compounds because in these experiments the rate of OH generation from the gas phase chemistry and the heterogeneous wall reactions may be comparable. There also appears to be significant variability in the chamber radical source strength which makes it very difficult to accurately model slowly reacting organic compounds.

The chamber walls may also act as sources of $NO_2$. Small $NO_x$ off-gassing rates are used to model the chamber environment. The rate of $NO_x$ off-gassing is determined from the peroxyacetylnitrate (PAN) yields in acetaldehyde - air experiments. The $NO_x$ off-gassing is only important in modeling experiments with low initial $NO_x$ concentrations. If this process is ignored in modeling low $NO_x$ experiments, the model calculations consistently underpredict the observed maximum ozone.

Two other important chamber effects are the deposition of ozone on the chamber walls which is fairly easily determined from dark ozone decay experiments and the heterogeneous hydrolysis of nitrogen pentoxide ($N_2O_5$) which leads to nitric acid formation. Rates for the later have been determined by Tuazon et al. (1983). The rates for both of these processes effect the computed ozone yields in the model simulations.

In summary, while environmental chambers are the best available systems for generating data to test the chemical mechanism, they are far from ideal because of uncertainty in processes occurring on the walls and the uncertainty in the light intensity and spectral distribution within the chambers. The detailed formulation of the chamber effects model and the sensitivity of the computed concentrations to key parameters in the chamber effects model are described in Carter et al. (1986).

## The Mechanism Evaluation

The performance measures employed in the evaluation are the relative and absolute errors in the maximum ozone concentrations and the $NO_x$ oxidation rate. The latter is assessed using the average rate of change of ozone minus NO [ie., d([O3]-[NO])/dt in ppb/minute] during the first half of the period required to reach ozone maximum. This rate is an indirect measure of the rate of $NO_x$ oxidation by organic species via the alkyl peroxy and acyl peroxy species. Other measures of model performance include the relative and absolute errors in the maximum PAN and aldehyde concentration, and in the half-lives of the organic precursors.

The protocol used to test the chemical mechanism incorporates several unique elements. First, where practical, all reactants in the experiments were represented by explicit chemical reactions in the mechanism. The major exception to this was the auto exhaust simulations which have too many species for this approach to be feasible. Second, a consistent set of assumptions were used in modeling all runs. Run-to-run adjustments of uncertain parameters to optimize fits to the data were not allowed. Adjustments of mechanistic and chamber effects parameters were developed only using the most appropriate runs for the particular parameter and then incorporated on a global basis into the testing program. Third, poorly understood chamber effects were represented as simply as possible. The minimum number of parameters needed to describe the data were incorporated into the parameterizations. Fourth, and very important, a large number of runs were used to evaluate the performance of the mechanism. Only runs which had major gaps in critical input data were eliminated from the testing data base. The use of a large number of runs is important because, now that the mechanism has been applied to many experiments, it is clear that their is some inherent variability in the data. Thus, the performance information based on simulating a small number of runs or

only runs from one chamber may not be meaningful. Fortunately, there is a large number of experiments for propene, toluene, n-butane, and surrogate mixtures that can be used to reliably evaluate the mechanism.

The evaluation was performed using environmental chamber data from four facilities:

- UCR - SAPRC 5800-liter Indoor Evacuable Chamber (EC)
- UCR - SAPRC 6400-liter Indoor Teflon Chamber (ITC)
- UCR - SAPRC 50,000-liter Outdoor Teflon Chamber (OTC)
- UNC 30,000-liter Outdoor Teflon Chamber (UNC)

The number of type of chamber runs used in the evaluation are summarized in Table II. This shows that almost 500 experiments were used in the testing. About 175 of these experiments employed complex mixtures that were surrogates for the organics found in ambient air. The range of concentrations used in these experiments are equal to and greater than those commonly observed in urban areas. The initial $NO_x$ generally exceeds 100 ppb and the initial NMOC generally exceeds 500 ppbC.

The evaluation was carried out in three steps. The first step involved modeling chamber characterization experiments to estimate the chamber effect parameters. Pure air, $NO_x$-air, NOx-CO-air, formaldehyde-air, and acetaldehyde-air experiments were used in this step. The second step involved modeling single organic-$NO_x$ experiments to test and refine the mechanisms for the organic precursors in the mechanism. The third step involved modeling organic mixtures in the presence of NOx. The synthetic mixtures were subdivided into simple and complex mixtures, where the former has species from one or two of the three major classes of organics (alkanes, alkenes, and aromatics) and the latter has species from all three major classes of organics. Simulations of auto exhaust experiments and dynamic injection

experiments were also included in the testing. The model performance statistics for maximum ozone are shown in Table III.

The model performance in the $NO_x$-air and CO-air simulations is shown in Figure 1. The predicted and observed change in [NO] and [$NO_2$] concentrations over the course of the runs are shown in the figure. These measure are used because very little ozone is formed in these high $NO_x$ characterization runs. The figure show the agreement for the change in NO and $NO_2$ concentrations are within about ±20% for all of the cases. This indictes the inorganic chemical reactions included in the mechanism reasonably accurate.

The predicted and observed maximum ozone concentrations and d([O3]-[NO])/dt are shown in Figures 2 through 5 for the single oxygenate, alkene, alkane and aromatic simulations, respectively. Examples of the distribution of errors in maximum ozone and the timing parameter for propene, n-butane, and toluene are shown in Figures 6 and 7. The results for the oxygenates, alkenes and aromatics show the maximum ozone and timing parameter predictions are within ±30% of the observed in almost all cases. The distribution of errors for propene and toluene show the errors are somewhat normally distributed about zero error. This level of agreement i, consider quite good. The results for the alkane simulations show a large amount of scatter and indicate unsatisfactory model performance. The alkanes are the least reactive compounds in the mechanism and the simulations of their oxidation are very sensitive to the chamber characterization procedures, in particular, the rate of radical off-gassing from the chamber walls. The uncertainty in the chamber effects makes it almost impossible to unambiguously evaluate the alkane mechanism at this time.

The predicted and observed maximum ozone concentrations and d([O3]-[NO])/dt are shown in Figures 8 through 10 for the simple synthetic mixtures, complex surrogate mixtures, and the auto exhaust

irradiations. The distribution of errors in the ozone maxima and timing parameter are shown in Figures 11 and 12. The results for the simple mixtures show most of the maximum ozone predictions agree with the observed values within ±30%. However, there are several mixed alkene runs from the EC that show greater than 30% underprediction of the ozone yield. The results for the complex surrogate mixtures show the vast majority of runs have better than ±30% agreement on the maximum ozone concentrations and the timing parameter. The distribution of errors in the ozone is centered on zero and shows roughly equal numbers of over and under predictions. Similarly good performance is shown for the simulations of the auto exhaust experiments.

The average bias and error in the mechanism's ozone predictions for these experiments are shown in Table III. These data show the average bias and error in the oxygenate simulations is -5% and ±25%, respectively. The performance for formaldehyde runs is considerably better than those for higher aldehydes and ketones. The average error and bias for ozone in the alkene simulations is +3% and ±21%, respectively. The performance for ethene and propene is quite good; the performance for butenes is adequate. The average error and bias for the alkane runs are +46% and ±69%, respectively. The performance on n-butane experiments is better than this, but the performance on long-chain alkane experiments is much worse. These poor statistics reflect the difficulties in testing the alkane mechanism discussed above. The average bias and error for the single aromatic runs are surprisingly small, +1% and ±19%, respectively. This good performance reflects the fact that the mechanism was optimized to fit most of the data. The statistics indicate the toluene mechanism has a tendency to overpredict ozone, whereas, the m-xylene and mesitylene mechanisms have tendencies to underpredict ozone yields on the average. Overall, for all single organic-$NO_x$ runs, the mechanism overpredicts by 12% and the average error is ±33%.

The average bias and error for the simulations of mixtures indicate reasonably good model performance. The results for the simple mixtures show +10% bias and ±35%. The results for the mini- and full-surrogate complex mixtures are better, since the average error is only ±23%. For the auto exhaust runs, the average bias is -11% and the average error is ±15%. This is the smallest average error of all the groups, which is rather ironic since speciation of the organics in the auto exhaust runs was the least certain of any group of experiments in the data base. Overall, for all organic mixture simulations, the performance statistics indicate the mechanism overpredicts ozone maxima by 4%, and the average error in the predictions are ±24%. Given the kinetic and mechanistic uncertainties as well as chamber characterization uncertainties, this level of performance is quite satisfactory.

Another important aspect of the evaluation consisted of searching for systematic biases in the mechanism. The error in the ozone was plotted against the $NO_x$ NMOC, and NMOC/$NO_x$ to investigate potential systematic errors. An example showing the error in the surrogate mixture runs versus the log of the NMOC/$NO_x$ ratio is illustrated in Figure 13. The distribution of errors appear to be fairly random for most of the range of NMOC/NOx ratio for which there are experimental data. The errors are totally random for NMOC/$NO_x$ ratios between 3 and 30. This indicates there is no apparent relationship between the error in the prediction and this important ratio for the range of the initial NMOC/$NO_x$ ratio commonly occurring in ambient air. However, above a NMOC/$NO_x$ ratio of 30, the mechanism consistently overpredicts ozone by a small amount. This small bias is not considered significant, especially since all of the high NMOC/$NO_x$ data are from one chamber.

The mechanism's predictive abilities for PAN and aldehydes were also examined in the evaluation. Figure 14 shows the predicted and observed PAN concentrations in the surrogate mixture runs. This shows that only about half of the predicted PAN maxima are within ±30% of the

observed. Figures 15 and 16 show the relative error in the PAN maxima for the propene, n-butane, toluene, simple mixture, complex surrogate mixture, and auto exhaust runs. These show fairly broad distribution of errors. Thus, the the mechanism's predictions for PAN are clearly less accurate than its predictions for ozone. Figure 17 shows the distribution of the relative errors in the maximum formaldehyde concentrations for the propene, simple mixture, and complex surrogate mixture runs. These distributions indicate fairly poor fits between the mechanism and the data. In this case, the discrepancies probably reflect uncertainties in the mechanism and the data as discussed in Carter et al. (1986).

## Conclusions

This mechanism evaluation is the most comprehensive study of its type on atmospheric chemical mechanisms. The evaluation is unique in that one mechanism was tested over a wide range conditions using data from a large number of experiments. Consistent chamber characterization procedures were employed and run-to-run adjustments of uncertain parameters were not permitted. Statistics on model performance were tabulated and displayed graphically. The performance data was examined closely for evidence of systematic biases.

The results of the mechanism evaluation indicate the mechanism is able to predict the rate of $NO_x$ oxidation and maximum ozone concentrations with little bias and within ±30% error for a large number of single organic-$NO_x$ experiments and organic mixture-$NO_x$ experiments. The results are statistically significant for propene, toluene, n-butane and a large number of mixtures including auto exhaust for which there are many experiments. However, there are probably an insufficient number of experiments for the results for aldehydes, ketones, butenes, C5+ alkanes, and aromatics other than toluene to be statistically significant. The ozone predictions for single organic-$NO_x$ irradiations

with carbonyls, alkenes, and aromatics show good agreement with the data on the average. The results for alkanes are not satisfactory. They show a large amount of error. The uncertainty in chamber characterization procedures strongly effect the predictions for alkanes-$NO_x$ mixtures. Because of these uncertainties, the alkane mechanism can not be evaluated without ambiguity at this time. With the exception of the single alkane runs, the results show that the mechanism's bias is generally less than 10%. On the surrogate mixture and auto exhaust runs, which are most representative of the types of mixtures for which the mechanism will be applied in atmospheric modeling, the average errors in the the maximum ozone are ±23% and ±15%, respectively. This level of performance is good considering the uncertainties in both the chemistry and chamber characterization.

Model performance for other intermediate species such as formaldehyde and peroxyacetylnitrate (PAN) is considerably worse than the performance for ozone; however, the data may not be reliable for these species.

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TABLE I. DETAILED CHEMICAL MECHANISM

| | REACTION | MOLECULE-CC-SEC (298 K) | PPM-MIN (298 K) | EXPRESSION |
|---|---|---|---|---|
| 1. | NO2 + HV ---> NO + O | RADIATION DEPENDENT | | |
| 2. | O + O2 + M ---> O3 + M | 6.12E-34 | 2.23E-05 | 3.00E-28/(T**2.3) |
| 3. | O + NO2 ---> NO + O2 | 9.30E-12 | 1.37E+04 | |
| 4. | O + NO2 + M ---> NO3 + M | 9.12E-32 | 3.32E-03 | 8.10E-27/(T**2.0) |
| 5. | NO + O3 ---> NO2 + O2 | 1.81E-14 | 2.68E+01 | 1.80E-12*EXP( -1370/T) |
| 6. | NO2 + O3 ---> NO3 + O2 | 3.23E-17 | 4.77E-02 | 1.20E-13*EXP( -2450/T) |
| 7. | NO + NO3 ---> 2.NO2 | 1.86E-11 | 2.75E+04 | 8.00E-12*EXP( 252/T) |
| 8. | NO + NO + O2 ---> 2.NO2 | 1.95E-38 | 7.09E-10 | 3.30E-39*EXP( 529/T) |
| 9. | NO2 + NO3 ---> N2O5 | 1.17E-12 | 1.73E+03 | SEE NOTE 1 |
| 10. | N2O5 ---> NO2 + NO3 | 3.47E-02 | 2.08E+00 | 1.06E 27*EXP(-11354/T)*(300/T)*R9 |
| 11. | N2O5 + H2O ---> 2.HNO3 | 1.00E-21 | 1.48E-06 | |
| 12. | NO2 + NO3 ---> NO + NO2 + O2 | 4.04E-16 | 5.98E-01 | 2.50E-14*EXP( -1229/T) |
| 13. | NO3 + HV ---> NO + O2 | RADIATION DEPENDENT | | |
| 14. | NO3 + HV ---> NO2 + O | RADIATION DEPENDENT | | |
| 15. | O3 + HV ---> O + O2 | RADIATION DEPENDENT | | |
| 16. | O3 + HV ---> O*SD + O2 | RADIATION DEPENDENT | | |
| 17. | O*SD + H2O ---> 2.OH | 2.20E-10 | 3.25E+05 | |
| 18. | O*SD + M ---> O + M | 2.90E-11 | 4.29E+04 | |
| 19. | NO + OH ---> HONO | 6.73E-12 | 9.94E+03 | SEE NOTE 1 |
| 20. | HONO + HV ---> NO + OH | RADIATION DEPENDENT | | |
| 21. | NO2 + H2O ---> HONO - NO2 + HNO3 | 4.00E-24 | 5.91E-09 | |
| 22. | NO2 + OH ---> HNO3 | 1.16E-11 | 1.71E+04 | SEE NOTE 1 |
| 23. | HNO3 + OH ---> NO3 | 1.28E-13 | 1.89E+02 | 9.40E-15*EXP( 778/T) |
| 24. | CO + OH ---> HO2 | 2.18E-13 | 3.22E+02 | |
| 25. | O3 + OH ---> HO2 + O2 | 6.78E-14 | 1.00E+02 | 1.60E-12*EXP( -942/T) |
| 26. | NO + HO2 ---> NO2 + OH | 8.28E-12 | 1.22E+04 | 3.70E-12*EXP( 240/T) |
| 27. | NO2 + HO2 ---> HNO4 | 1.39E-12 | 2.05E+03 | SEE NOTE 1 |
| 28. | HNO4 ---> NO2 + HO2 | 8.41E-02 | 5.05E 00 | 4.29E 26*EXP(-10876/T)*R27 |
| 29. | HNO4 + OH ---> NO2 + H2O + O2 | 4.00E-12 | 5.91E+03 | |
| 30. | O3 + HO2 ---> OH + 2.O2 | 2.01E-15 | 2.96E+00 | 1.40E-14*EXP( -579/T) |
| 31. | HO2 + HO2 ---> H2O2 + O2 | 1.76E-12 | 2.59E+03 | 2.20E-13*EXP( 619/T) |
| 32. | HO2 + HO2 + M ---> H2O2 + O2 | 5.13E-32 | 1.87E-03 | 1.90E-33*EXP( 982/T) |
| 33. | HO2 + HO2 + H2O ---> H2O2 + O2 + H2O | 3.96E-30 | 1.44E-01 | 3.10E-34*EXP( 2818/T) |
| 34. | HO2 + HO2 + H2O ---> H2O2 + O2 + H2O | 2.84E-30 | 1.04E-01 | 6.60E-35*EXP( 3180/T) |
| 35. | NO3 + HO2 ---> HNO3 + O2 | 1.76E-12 | 2.59E+03 | 2.20E-13*EXP( 619/T) |
| 36. | NO3 + HO2 + M ---> HNO3 + O2 | 5.13E-32 | 1.87E-03 | 1.90E-33*EXP( 982/T) |
| 37. | NO3 + HO2 + H2O ---> HNO3 + O2 + H2O | 3.96E-30 | 1.44E-01 | 3.10E-34*EXP( 2818/T) |
| 38. | NO3 + HO2 + H2O ---> HNO3 + O2 + H2O | 2.84E-30 | 1.04E-01 | 6.60E-35*EXP( 3180/T) |
| 39. | H2O2+ HV ---> 2.OH | RADIATION DEPENDENT | | |
| 40. | H2O2+ OH ---> HO2 + H2O | 1.66E-12 | 2.45E+03 | 3.10E-12*EXP( -187/T) |
| 41. | RO2 + NO ---> NO | 7.68E-12 | 1.14E+04 | 4.20E-12*EXP( 180/T) |
| 42. | RCO3 + NO ---> NO | 7.68E-12 | 1.14E+04 | 4.20E-12*EXP( 180/T) |
| 43. | RCO3 + NO2 ---> NO2 | 5.12E-12 | 7.57E+03 | 2.80E-12*EXP( 180/T) |
| 44. | RO2 + HO2 ---> HO2 | 3.00E-12 | 4.43E+03 | |
| 45. | RCO3 + HO2 ---> HO2 | 3.00E-12 | 4.43E+03 | |
| 46. | ROOH + HV ---> HO2 + OH | RADIATION DEPENDENT | | |

TABLE I. DETAILED CHEMICAL MECHANISM (CONTINUED)

| | REACTION | MOLECULE-CC-SEC (298 K) | PPM-MIN (298 K) | EXPRESSION |
|---|---|---|---|---|
| 47. | RO2 + RO2 ---> | 1.00E-15 | 1.48E+00 | |
| 48. | RO2 + RCO3 ---> | 3.00E-12 | 4.43E+03 | |
| 49. | RCO3 + RCO3 ---> | 2.50E-12 | 3.69E+03 | |
| 50. | HCHO + HV ---> 2.HO2 + CO | RADIATION DEPENDENT | | |
| 51. | HCHO + HV ---> CO + H2 | RADIATION DEPENDENT | | |
| 52. | HCHO + OH ---> HO2 + CO + H2O | 9.00E-12 | 1.33E+04 | |
| 53. | HCHO + HO2 ---> RO2R + RO2 | 1.00E-14 | 1.48E+01 | |
| 54. | HCHO + NO3 ---> HNO3 + HO2 + CO | 5.97E-16 | 8.82E-01 | 6.00E-13*EXP( -2060/T) |
| 55. | ALD2 + OH ---> MCO3 + H2O + RCO3 | 1.60E-11 | 2.36E+04 | 6.90E-12*EXP( 250/T) |
| 56. | ALD2 + HV ---> CO + RO2R + HO2 + RO2 + HCHO | RADIATION DEPENDENT | | |
| 57. | ALD2 + NO3 ---> HNO3 + MCO3 + RCO3 | 2.50E-15 | 3.69E+00 | 3.00E-13*EXP( -1427/T) |
| 58. | MCO3 + NO ---> NO2 + RO2R + RO2 + HCHO | 7.68E-12 | 1.14E+04 | 4.20E-12*EXP( 180/T) |
| 59. | MCO3 + NO2 ---> PAN | 5.12E-12 | 7.57E+03 | 2.80E-12*EXP( 180/T) |
| 60. | MCO3 + HO2 ---> ROOH + HCHO | 3.00E-12 | 4.43E+03 | |
| 61. | MCO3 + RO2 ---> .5HO2 + HCHO + RO2 | 3.00E-12 | 4.43E+03 | |
| 62. | MCO3 + RCO3 ---> HO2 + HCHO + RCO3 | 2.50E-12 | 3.69E+03 | |
| 63. | PAN ---> MCO3 + NO2 + RCO3 | 3.68E-04 | 2.21E-02 | 2.00E+16*EXP(-13542/T) |
| 64. | RCHO + OH ---> RCO3 + PCO3 | 1.98E-11 | 2.93E+04 | 8.50E-12*EXP( 252/T) |
| 65. | RCHO + HV ---> RO2R + HO2 + CO + RO2 + ALD2 | RADIATION DEPENDENT | | |
| 66. | RCHO + NO3 ---> HNO3 + PCO3 + RCO3 | 2.46E-15 | 3.63E+00 | 3.00E-13*EXP( -1432/T) |
| 67. | PCO3 + NO ---> RO2R + NO2 + RO2 + ALD2 | 7.68E-12 | 1.14E+04 | 4.20E-12*EXP( 180/T) |
| 68. | PCO3 + NO2 ---> PPN | 5.12E-12 | 7.57E+03 | 2.80E-12*EXP( 180/T) |
| 69. | PCO3 + HO2 ---> ROOH + ALD2 | 3.00E-12 | 4.43E+03 | |
| 70. | PCO3 + RO2 ---> .5HO2 + ALD2 + RO2 | 3.00E-12 | 4.43E+03 | |
| 71. | PCO3 + RCO3 ---> HO2 + ALD2 + RCO3 | 2.50E-12 | 3.69E+03 | |
| 72. | PPN ---> PCO3 + NO2 + RCO3 | 3.68E-04 | 2.21E-02 | 2.00E+16*EXP(-13542/T) |
| 73. | ACET + HV ---> MCO3 + RO2R + RCO3 + RO2 + HCHO | RADIATION DEPENDENT | | |
| 74. | ACET + OH ---> RO2R + RO2 + MGLY | 2.29E-13 | 3.39E+02 | 1.00E-11*EXP( -1125/T) |
| 75. | MEK + HV ---> MCO3 + RO2R + RCO3 + RO2 + ALD2 | RADIATION DEPENDENT | | |
| 76. | MEK + OH ---> MKO2 + .5R2O2 + 1.5RO2 + .5HCHO + .5ALD2 | 9.85E-13 | 1.46E+03 | 1.20E-11*EXP( -745/T) |
| 77. | MKO2 + NO ---> NO2 + .5MCO3 + .5PCO3 + RCO3 | 7.68E-12 | 1.14E+04 | 4.20E-12*EXP( 180/T) |
| 78. | MKO2 + HO2 ---> ROOH + .5HCHO + .5ALD2 | 3.00E-12 | 4.43E+03 | |
| 79. | MKO2 + RO2 ---> .5HO2 + .5HCHO + .5ALD2 + RO2 | 1.00E-15 | 1.48E+00 | |
| 80. | MKO2 + RCO3 ---> .5HO2 + .5HCHO + .5ALD2 + RCO3 | 3.00E-12 | 4.43E+03 | |
| 81. | GLYX + HV ---> .13HCHO +1.87CO | RADIATION DEPENDENT | | |
| 82. | GLYX + OH ---> .63HO2 +1.26CO + .37GCO3 + .37RCO3 | 1.15E-11 | 1.70E+04 | |
| 83. | GLYX + NO3 ---> HNO3 + .63HO2 +1.26CO + .37GCO3 + .37RCO3 | 6.01E-16 | 8.88E-01 | 6.00E-13*EXP( -2058/T) |
| 84. | GCO3 + NO2 ---> GPAN | 5.12E-12 | 7.57E+03 | 2.80E-12*EXP( 180/T) |
| 85. | GCO3 + NO ---> NO2 + HO2 + CO | 7.68E-12 | 1.14E+04 | 4.20E-12*EXP( 180/T) |
| 86. | GPAN ---> GCO3 + NO2 + RCO3 | 3.68E-04 | 2.21E-02 | 2.00E+16*EXP(-13542/T) |
| 87. | GCO3 + HO2 ---> ROOH + CO | 3.00E-12 | 4.43E+03 | |
| 88. | GCO3 + RO2 ---> .5HO2 + CO + RO2 | 3.00E-12 | 4.43E+03 | |
| 89. | GCO3 + RCO3 ---> HO2 + CO + RCO3 | 2.50E-12 | 3.69E+03 | |
| 90. | MGLY + HV ---> MCO3 + HO2 + CO + RCO3 | RADIATION DEPENDENT | | |
| 91. | MGLY + OH ---> MCO3 + CO + RCO3 | 1.70E-11 | 2.51E+04 | |
| 92. | MGLY + NO3 ---> HNO3 + MCO3 + CO + RCO3 | 2.50E-15 | 3.69E+00 | 3.00E-13*EXP( -1427/T) |

TABLE I. DETAILED CHEMICAL MECHANISM (CONTINUED)

| | REACTION | MOLECULE-CC-SEC (298 K) | PPM-MIN (298 K) | EXPRESSION |
|---|---|---|---|---|
| 93. | GCHO + HV ---> HCHO + 2.HO2 + CO | RADIATION DEPENDENT | | |
| 94. | GCHO + OH ---> GAO3 + RCO3 | 2.30E-11 | 3.40E+04 | |
| 95. | GCHO + NO3 ---> HNO3 + GAO3 + RCO3 | 2.50E-15 | 3.69E+00 | 3.00E-13*EXP( -1427/T) |
| 96. | GAO3 + NO2 ---> PANG | 5.12E-12 | 7.57E+03 | 2.80E-12*EXP( 180/T) |
| 97. | GAO3 + NO ---> NO2 + HO2 + HCHO | 7.68E-12 | 1.14E+04 | 4.20E-12*EXP( 180/T) |
| 98. | PANG ---> GAO3 + NO2 + RCO3 | 3.68E-04 | 2.21E-02 | 2.00E+16*EXP(-13542/T) |
| 99. | GAO3 + HO2 ---> ROOH + HCHO | 3.00E-12 | 4.43E+03 | |
| 100. | GAO3 + RO2 ---> .5HO2 + HCHO + RO2 | 3.00E-12 | 4.43E+03 | |
| 101. | GAO3 + RCO3 ---> HO2 + HCHO + RCO3 | 2.50E-12 | 3.69E+03 | |
| 102. | ALK3 + OH ---> RO2R + RO2 + .31RCHO + .69ACET | 1.18E-12 | 1.75E+03 | 1.27E-17*EXP(14/T)*T**2. |
| 103. | ALK4 + OH ---> B01*HCHO +B02*ALD2 +B03*RCHO +B04*ACET +B05*MEK +B06*RO2N +B07*RO2R +B08*R2O2 +B09*RO2 | 3.22E-12 SEE NOTE 2 | 4.76E+03 | 1.05E-11*EXP( -353/T) |
| 104. | ALK7 + OH ---> B10*HCHO +B11*ALD2 +B12*RCHO +B13*ACET +B14*MEK +B15*RO2N +B16*RO2R +B17*R2O2 +B18*RO2 | 6.16E-12 SEE NOTE 2 | 9.11E+03 | 1.62E-11*EXP( -288/T) |
| 105. | ALKN + OH ---> NO2 +.155MEK +1.05RCHO + .48ALD2 + .16HCHO +1.39R2O2 +1.39RO2 | 2.03E-12 | 3.00E+03 | 2.19E-11*EXP( -709/T) |
| 106. | RO2N + NO ---> ALKN | 7.68E-12 | 1.14E+04 | 4.20E-12*EXP( 180/T) |
| 107. | RO2N + HO2 ---> ROOH + MEK | 3.00E-12 | 4.43E+03 | |
| 108. | RO2N + RO2 ---> RO2 + .5HO2 + MEK | 1.00E-15 | 1.48E+00 | |
| 109. | RO2N + RCO3 ---> RCO3 + .5HO2 + MEK | 3.00E-12 | 4.43E+03 | |
| 110. | R2O2 + NO ---> NO2 | 7.68E-12 | 1.14E+04 | 4.20E-12*EXP( 180/T) |
| 111. | R2O2 + HO2 ---> ROOH | 3.00E-12 | 4.43E+03 | |
| 112. | R2O2 + RO2 ---> RO2 | 1.00E-15 | 1.48E+00 | |
| 113. | R2O2 + RCO3 ---> RCO3 | 3.00E-12 | 4.43E+03 | |
| 114. | RO2R + NO ---> NO2 + HO2 | 7.68E-12 | 1.14E+04 | 4.20E-12*EXP( 180/T) |
| 115. | RO2R + HO2 ---> ROOH | 3.00E-12 | 4.43E+03 | |
| 116. | RO2R + RO2 ---> RO2 + .5HO2 | 1.00E-15 | 1.48E+00 | |
| 117. | RO2R + RCO3 ---> RCO3 + .5HO2 | 3.00E-12 | 4.43E+03 | |
| 118. | ETHE + OH ---> RO2R + RO2 +1.56HCHO + .22GCHO | 8.54E-12 | 1.26E+04 | 2.15E-12*EXP( 411/T) |
| 119. | ETHE + O3 ---> HCHO + .12HO2 + .42CO | 1.74E-18 | 2.57E-03 | 1.20E-14*EXP( -2634/T) |
| 120. | ETHE + O ---> RO2R + HO2 + CO + RO2 + HCHO | 7.29E-13 | 1.08E+03 | 1.04E-11*EXP( -792/T) |
| 121. | ETHE + NO3 ---> R2O2 + RO2 + NO2 + 2.HCHO | 1.10E-16 | 1.62E-01 | 2.00E-12*EXP( -2923/T) |
| 122. | PRPE + OH ---> HCHO + RO2 + RO2R + ALD2 | 2.63E-11 | 3.89E+04 | 4.85E-12*EXP( 504/T) |
| 123. | PRPE + O3 ---> .65HCHO + .5ALD2 +.165HO2 +.285CO + .06OH +.135RO2R +.135RO2 | 1.13E-17 | 1.67E-02 | 1.32E-14*EXP( -2105/T) |
| 124. | PRPE + O ---> .6ACET + .6RO2R + .2ALD2 + .2HO2 + .6RO2 + .4CO + .4HCHO | 3.98E-12 | 5.88E+03 | 1.18E-11*EXP( -324/T) |
| 125. | PRPE + NO3 ---> R2O2 + RO2 + HCHO + ALD2 + NO2 | 7.57E-15 | 1.12E+01 | 5.00E-12*EXP( -1935/T) |
| 126. | OBUT + OH ---> RO2R + RO2 + HCHO + RCHO | 3.14E-11 | 4.64E+04 | 6.53E-12*EXP( 468/T) |
| 127. | OBUT + O3 ---> .5HCHO + .5RCHO +.165HO2 + .15ALD2 + .06OH +.135RO2R +.135RO2 | 1.10E-17 | 1.63E-02 | 3.46E-15*EXP( -1713/T) |
| 128. | OBUT + O ---> .44MEK + .39RCHO + .34HO2 + .17HCHO + .17CO + .17ALD2 | 4.19E-12 | 6.19E+03 | 1.25E-11*EXP( -326/T) |
| 129. | OBUT + NO3 ---> RO2R + RO2 + HCHO + RCHO + NO2 | 9.67E-15 | 1.43E+01 | 5.00E-12*EXP( -1862/T) |
| 130. | TBUT + OH ---> RO2R + RO2 + 2.ALD2 | 6.37E-11 | 9.42E+04 | 1.01E-11*EXP( 549/T) |
| 131. | TBUT + O3 ---> ALD2 + .27RO2R + .12OH + .21HO2 + .3HCHO + .15CO + .27RO2 | 2.00E-16 | 2.96E-01 | 9.08E-15*EXP( -1137/T) |

TABLE I. DETAILED CHEMICAL MECHANISM (CONTINUED)

| | REACTION | MOLECULE-CC-SEC (298 K) | PPM-MIN (298 K) | EXPRESSION |
|---|---|---|---|---|
| 132. | TBUT + O ---> MEK + .4HO2 | 2.34E-11 | 3.45E+04 | 2.26E-11*EXP( 10/T) |
| 133. | TBUT + NO3 ---> R2O2 + RO2 + NO2 + 2.ALD2 | 3.79E-13 | 5.61E+02 | 1.00E-11*EXP( -975/T) |
| 134. | IBUT + OH ---> RO2R + RO2 + HCHO + ACET | 5.14E-11 | 7.60E+04 | 9.51E-12*EXP( 503/T) |
| 135. | IBUT + O3 ---> .5ACET + .5HCHO + .4MEK + .06HO2 + .10OH + .10RO2R + .10RO2 + .10MGLY | 1.21E-17 | 1.78E-02 | 3.55E-15*EXP( -1694/T) |
| 136. | IBUT + O ---> .5MEK + .5RCHO + .4HO2 | 1.52E-11 | 2.25E+04 | 1.76E-11*EXP( -43/T) |
| 137. | IBUT + NO3 ---> R2O2 + RO2 + ACET + HCHO + NO2 | 2.69E-13 | 3.98E+02 | 1.00E-11*EXP( -1077/T) |
| 138. | BENZ + OH ---> .27PHEN + .27HO2 + .73RO2R + .73RO2 + .212GLYX + .65BGLY | 1.28E-12 | 1.90E+03 | 7.57E-12*EXP( -529/T) |
| 139. | BGLY + OH ---> GCO3 + RCO3 | 3.00E-11 | 4.43E+04 | |
| 140. | BGLY + HV ---> GCO3 + RCO3 + HO2 | RADIATION DEPENDENT | | |
| 141. | TOLU + OH ---> .16CRES + .16HO2 + .08BCHO + .114GLYX + .144MGLY + .40DIAL + .84RO2R + .84RO2 | 6.19E-12 | 9.14E+03 | 2.10E-12*EXP( 322/T) |
| 142. | DIAL + OH ---> PCO3 + RCO3 | 3.00E-11 | 4.43E+04 | |
| 143. | DIAL + HV ---> HO2 + CO + MCO3 + RCO3 | RADIATION DEPENDENT | | |
| 144. | XYLE + OH ---> .17CRES + .17HO2 + .04BCHO + .095GLYX + .83RO2 + .83RO2R + .316MGLY + .65DIAL | 2.45E-11 | 3.62E+04 | 1.66E-11*EXP( 116/T) |
| 145. | TMBZ + OH ---> .17CRES + .17HO2 + .02BCHO + .86MGLY + .83RO2 + .83RO2R + .49DIAL | 6.20E-11 | 9.16E+04 | |
| 146. | CRES + OH ---> .2MGLY + .15RO2P + .85RO2R + RO2 | 4.00E-11 | 5.91E+04 | |
| 147. | CRES + NO3 ---> HNO3 + BZO | 2.20E-11 | 3.25E+04 | |
| 148. | RO2P + NO ---> NPHE | 7.68E-12 | 1.14E+04 | 4.20E-12*EXP( 180/T) |
| 149. | RO2P + HO2 ---> ROOH | 3.00E-12 | 4.43E+03 | |
| 150. | RO2P + RO2 ---> RO2 + .5HO2 | 1.00E-15 | 1.48E+00 | |
| 151. | RO2P + RCO3 ---> RCO3 + .5HO2 | 3.00E-12 | 4.43E+03 | |
| 152. | PHEN + OH ---> .2GLYX + .15RO2P + .85RO2R | 2.80E-11 | 4.14E+04 | |
| 153. | PHEN + NO3 ---> HNO3 + BZO | 3.80E-12 | 5.62E+03 | |
| 154. | BZO + NO2 ---> NPHE | 1.50E-11 | 2.22E+04 | |
| 155. | BZO + HO2 ---> PHEN | 3.00E-12 | 4.43E+03 | |
| 156. | BZO ---> PHEN | 1.00E-03 | 6.00E-02 | |
| 157. | NPHE + NO3 ---> HNO3 + BZN2 | 3.80E-12 | 5.62E+03 | |
| 158. | BZN2 + NO2 ---> DNPH | 1.50E-11 | 2.22E+04 | |
| 159. | BZN2 + HO2 ---> NPHE | 3.00E-12 | 4.43E+03 | |
| 160. | BZN2 ---> NPHE | 1.00E-03 | 6.00E-02 | |
| 161. | BCHO + OH ---> BAO3 + RCO3 | 1.20E-11 | 1.77E+04 | |
| 162. | BCHO + HV ---> | RADIATION DEPENDENT | | |
| 163. | BCHO + NO3 ---> BAO3 + HNO3 + RCO3 | 1.95E-15 | 2.89E+00 | 3.00E-13*EXP( -1500/T) |
| 164. | BAO3 + NO ---> BZO + NO2 + RO2R + RO2 | 7.68E-12 | 1.14E+04 | 4.20E-12*EXP( 180/T) |
| 165. | BAO3 + NO2 ---> PBZN | 5.12E-12 | 7.57E+03 | 2.80E-12*EXP( 180/T) |
| 166. | PBZN ---> BAO3 + NO2 + RCO3 | 1.62E-04 | 9.74E-03 | 1.60E+15*EXP(-13033/T) |
| 167. | BAO3 + HO2 ---> ROOH + PHEN | 3.00E-12 | 4.43E+03 | |
| 168. | BAO3 + RO2 ---> .5HO2 + PHEN + RO2 | 3.00E-12 | 4.43E+03 | |
| 169. | BAO3 + RCO3 ---> HO2 + PHEN + RCO3 | 2.50E-12 | 3.69E+03 | |

TABLE I. DETALIED CHEMICAL MECHANISM (CONTINUED)

NOTES:

1. Pressure and temperature dependent rate constants are determined from the expression

$$K = \frac{B(T^{**}C)M}{1 + \frac{B(T^{**}C)M}{D(T^{**}E)}} A^{**}EE, \quad EE = \frac{1.}{1 + \left( LOG10\left(\frac{B(T^{**}C)M}{D(T^{**}E)}\right) \right)^{**}2}$$

Where:

| Reaction | A | B | C | D | E |
|---|---|---|---|---|---|
| 9 | 0.6 | 9.0E-20 | -4.3 | 2.4E-11 | -0.5 |
| 19 | 0.6 | 1.0E-22 | -3.3 | 9.0E-09 | -1.0 |
| 22 | 0.6 | 2.2E-22 | -3.2 | 4.0E-08 | -1.3 |
| 27 | .56 | 5.71E-20 | -4.6 | 1.34E-12 | 0.2 |

2. Alkane product coefficents are temperature dependent. They are determined by interpolation from the values at the following three temperatures.

| Coeff. | 270 K | 300 K | 330 K |
|---|---|---|---|
| B01 | 0.197 | 0.189 | 0.188 |
| B02 | 0.168 | 0.315 | 0.582 |
| B03 | 0.115 | 0.166 | 0.244 |
| B04 | 0.351 | 0.339 | 0.350 |
| B05 | 0.489 | 0.442 | 0.267 |
| B06 | 0.114 | 0.073 | 0.050 |
| B07 | 0.886 | 0.927 | 0.950 |
| B08 | 0.446 | 0.599 | 0.807 |
| B09 | 1.332 | 1.526 | 1.757 |
| B10 | 0.005 | 0.023 | 0.054 |
| B11 | 0.021 | 0.032 | 0.081 |
| B12 | 0.215 | 0.249 | 0.296 |
| B13 | 0.297 | 0.355 | 0.419 |
| B14 | 0.765 | 0.882 | 0.891 |
| B15 | 0.288 | 0.190 | 0.126 |
| B16 | 0.701 | 0.810 | 0.873 |
| B17 | 0.651 | 0.837 | 1.004 |
| B18 | 1.352 | 1.647 | 1.877 |

TABLE I. DETAILED CHEMICAL MECHANISM (CONTINUED)

| | SPECIES | ABREVIATION |
|---|---|---|
| 1. | NITRIC OXIDE | NO |
| 2. | NITROGEN DIOXIDE | NO2 |
| 3. | OZONE | O3 |
| 4. | NITROUS ACID | HONO |
| 5. | NITRIC ACID | HNO3 |
| 6. | PERNITRIC ACID | HNO4 |
| 7. | NITROGEN PENTOXIDE | N2O5 |
| 8. | NITROGEN TRIOXIDE | NO3 |
| 9. | HYDROPEROXY RADICAL | HO2 |
| 10. | HYDROGEN PEROXIDE | H2O2 |
| 11. | CARBON MONOXIDE | CO |
| 12. | FORMALDEHYDE | HCHO |
| 13. | ACETALDEHYDE | ALD2 |
| 14. | PROPIONALDEHYDE | RCHO |
| 15. | PEROXYACETYLNITRATE | PAN |
| 16. | PEROXYPROPIONYL NITRATE | PPN |
| 17. | TOTAL RO2 RADICALS | RO2 |
| 18. | TOTAL RCO3 RADICALS | RCO3 |
| 19. | ORGANIC PEROXIDE | ROOH |
| 20. | ACETONE | ACET |
| 21. | METHYL ETHYL KETONE | MEK |
| 22. | GLYOXAL | GLYX |
| 23. | GLYOXAL PAN | GPAN |
| 24. | METHYL GLYOXAL | MGLY |
| 25. | GLYCOL ALDEHYDE | GCHO |
| 26. | GLYCOL ALDEHYDE PAN | PANG |
| 27. | PROPANE | ALK3 |
| 28. | C4-C5 ALKANES | ALK4 |
| 29. | C6+ ALKANES | ALK7 |
| 30. | ALKYL NITRATES | ALKN |
| 31. | ETHENE | ETHE |
| 32. | PROPENE | PRPE |
| 33. | 1-BUTENE | OBUT |
| 34. | TRANS-2-BUTENE | TBUT |
| 35. | ISO-BUTENE | IBUT |
| 36. | BENZENE | BENZ |
| 37. | TOLUENE | TOLU |
| 38. | M-XYLENE | XYLE |
| 39. | 1,3,5 TRI-M-BENZENE | TMBZ |
| 40. | DICARBONYLS | DIAL |
| 41. | O-CRESOL | CRES |
| 42. | PHENOLS | PHEN |
| 43. | NITROPHENOLS | NPHE |
| 44. | DICARBONYLS | BGLY |
| 45. | BENZALDEHYDE | BCHO |
| 46. | BENZALDEHYDE PAN | PBZN |
| 47. | DI-NITROPHENOLS | DNPH |
| | STEADY STATE SPECIES | |
| 48. | OXYGEN - SINGLET D | O*SD |
| 49. | OXYGEN - ATOMIC | O |
| 50. | HYDROXYL RADICAL | OH |
| 51. | ACETALDEHYDE RCO3 | MCO3 |
| 52. | PROPIONALDEHYDE RCO3 | PCO3 |
| 53. | GLYOXAL RCO3 | GCO3 |
| 54. | GLYCOL ALDEHYDE RCO3 | GAO3 |
| 55. | GENERAL RO2 #1 | RO2R |
| 56. | GENERAL RO2 #2 | R2O2 |
| 57. | MEK RO2 | MKO2 |
| 58. | ALKYL NITRATE RO2 | RO2N |
| 59. | PHENOL RO2 | RO2P |
| 60. | BENZALDEHYDE N-RO2 | BZN2 |
| 61. | BENZALDEHYDE RCO3 | BAO3 |
| 62. | PHENOXY RADICAL | BZO |
| | CONSTANT SPECIES | |
| 63. | MOLECULAR OXYGEN | O2 |
| 64. | AIR | M |
| 65. | H2O VAPOR | H2O |

TABLE II

SUMMARY OF ENVIRONMENTAL CHAMBER RUNS USED FOR MECHANISM EVALUATION

| Type of Environmental Chamber Run | | Number of Runs | | | | |
|---|---|---|---|---|---|---|
| | | EC | ITC | OTC | UNC | All |
| Characterization | Various | 10 | 14 | 10 | 37 | 71 |
| Single Organic-$NO_x$ | Oxygenates | 7 | 1 | 2 | 15 | 25 |
| | Ethene | 6 | 2 | | 6 | 14 |
| | Propene | 15 | 7 | 5 | 22 | 49 |
| | Butenes | 6 | 5 | | 5 | 16 |
| | n-Butane | 14 | 5 | 1 | 7 | 27 |
| | >C4 Alkanes | 6 | 8 | | 6 | 20 |
| | Toluene | 13 | 2 | | 5 | 20 |
| | Other Aromatics | 7 | 13 | | 4 | 24 |
| Known Mixtures | Simple Mixtures | 22 | | | 18 | 40 |
| | Complex Mixtures | 11 | 45 | 62 | 33 | 151 |
| Auto Exhaust | Charger and Volare | | | | 25 | 25 |
| Dynamic Injection | Propene and Mixtures | | | | 9 | 9 |
| Total Number of Runs | | 117 | 102 | 80 | 192 | 491 |

TABLE III

AVERAGE MODEL PERFORMANCE FOR MAXIMUM OZONE

| Run Type | Bias (%)* | Error (%)* |
|---|---|---|
| Formaldehyde | -1 | 19 |
| Acetaldehyde | -26 | 26 |
| Other Carbonyls | +4 | 44 |
| All Carbonyls | -5 | 25 |
| Ethene | +2 | 18 |
| Propene | +3 | 18 |
| Butenes | +4 | 34 |
| All Alkenes | +3 | 21 |
| Butane | +31 | 67 |
| Branched Alkanes | +34 | 49 |
| Long-chain Alkanes | +83 | 84 |
| All Alkanes | +46 | 69 |
| Benzene | +3 | 5 |
| Toluene | +11 | 24 |
| Xylenes | -9 | 16 |
| Mesitylene | -11 | 21 |
| All Aromatics | +1 | 19 |
| All Single HC Runs | +12 | 33 |
| Simple Mixtures | +10 | 35 |
| Mini Surrogates | +10 | 22 |
| Full Surrogates | +3 | 23 |
| Auto Exhaust | -11 | 15 |
| All HC Mixtures | +4 | 24 |
| All Run Average | +7 | 28 |

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*Positive bias indicates model overprediction.

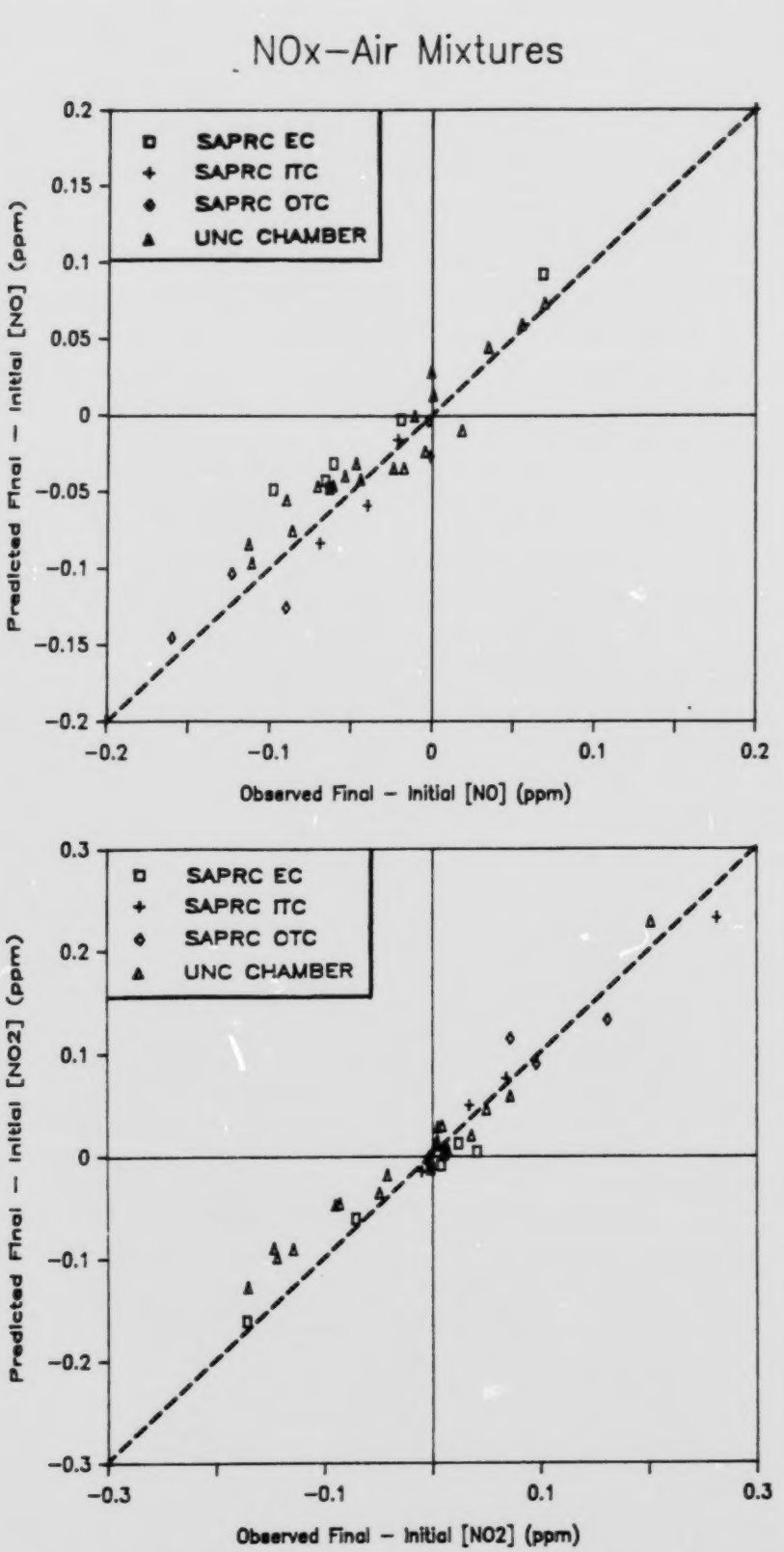


Figure 1. Predicted versus observed change in NO and $NO_2$ for $NO_x$-air and $NO_x$-CO-air characterization runs.

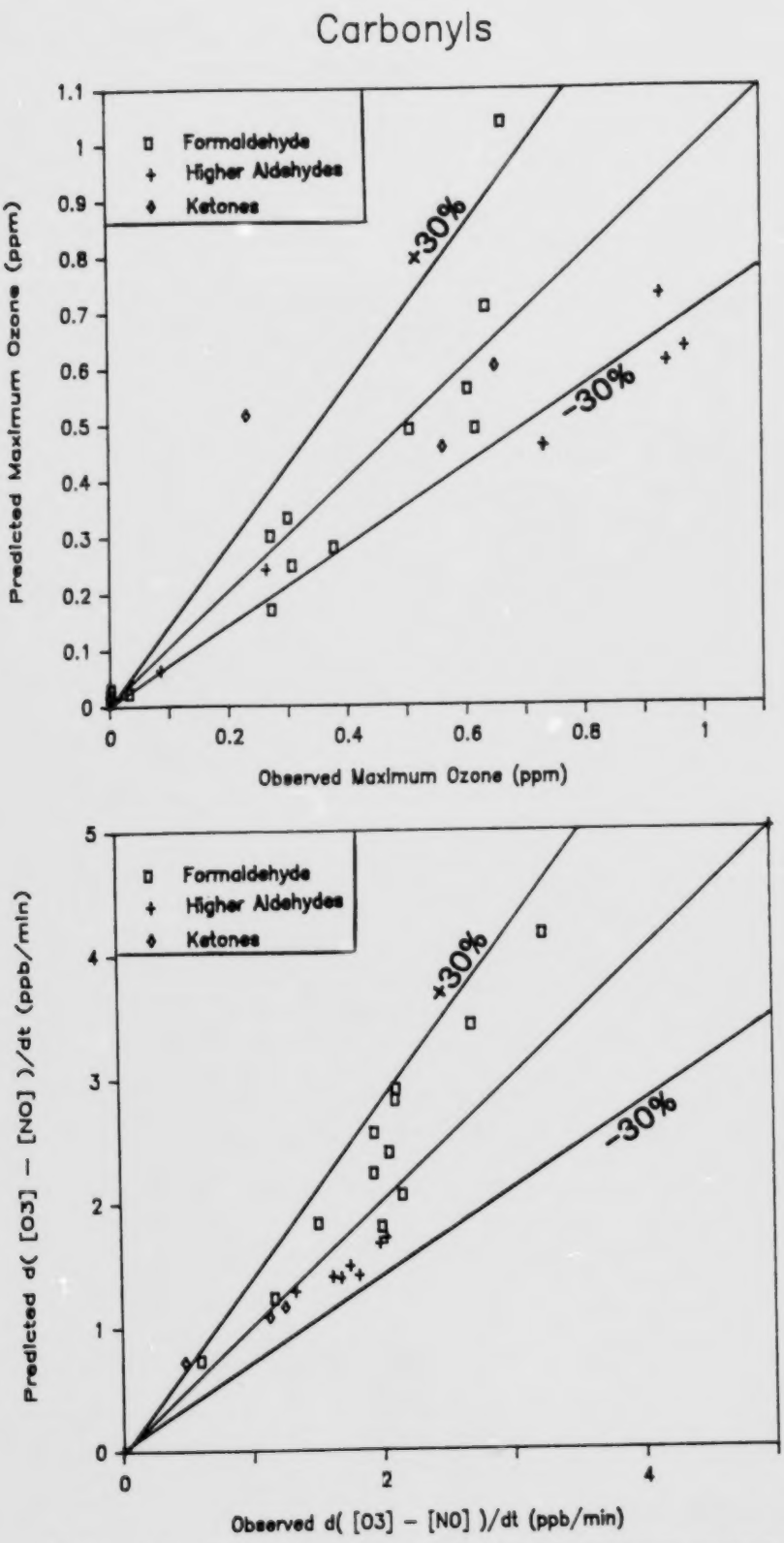


Figure 2. Predicted versus observed maximum ozone and $d([O_3]-[NO])/dt$ for carbonyl-$NO_x$ runs.

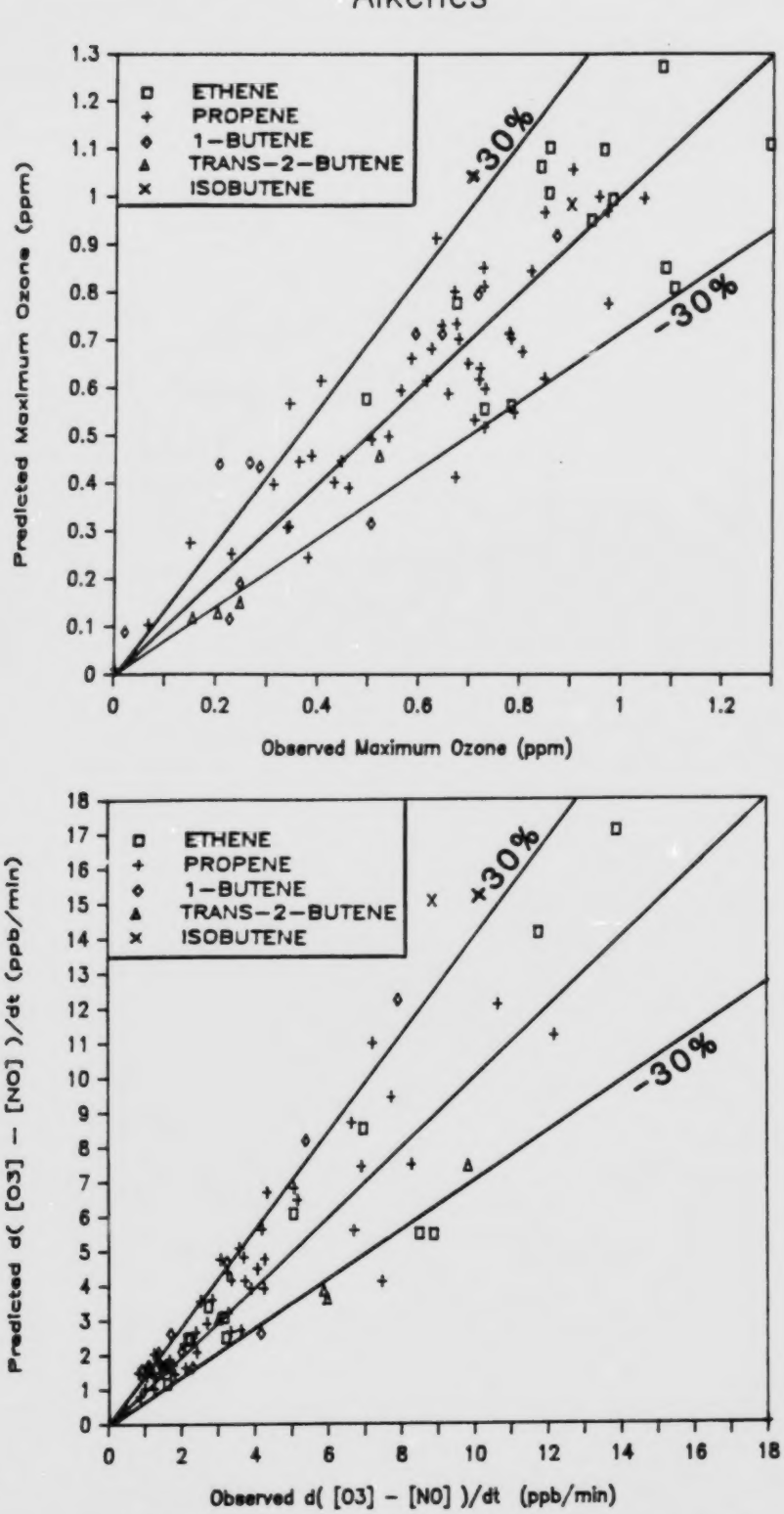


Figure 3. Predicted versus observed maximum ozone and $d([O_3]-[NO])/dt$ for alkene-$NO_x$ runs.

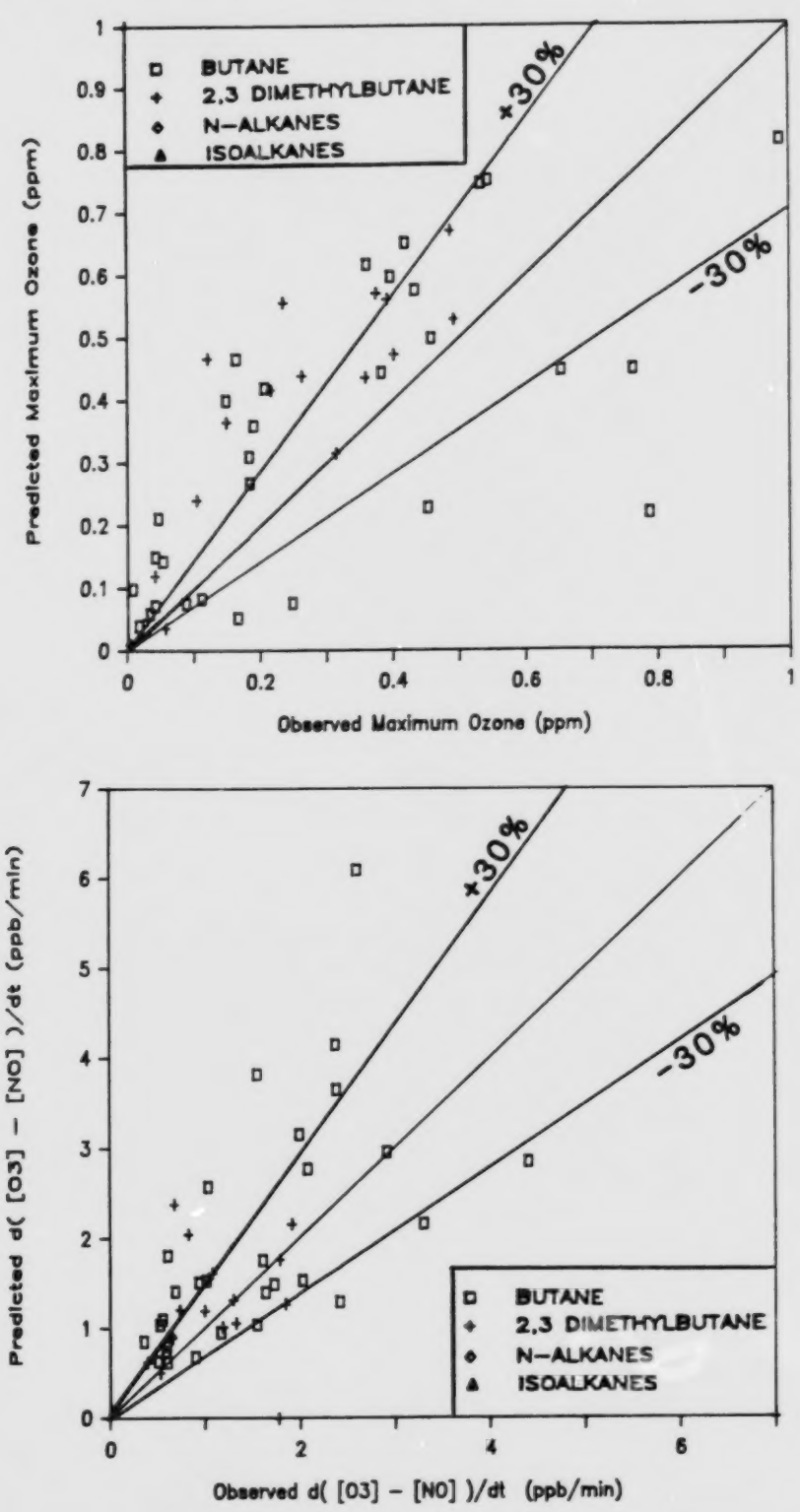


Figure 4. Predicted versus observed maximum ozone and $d([O_3]-[NO])/dt$ for alkane-$NO_x$ runs.

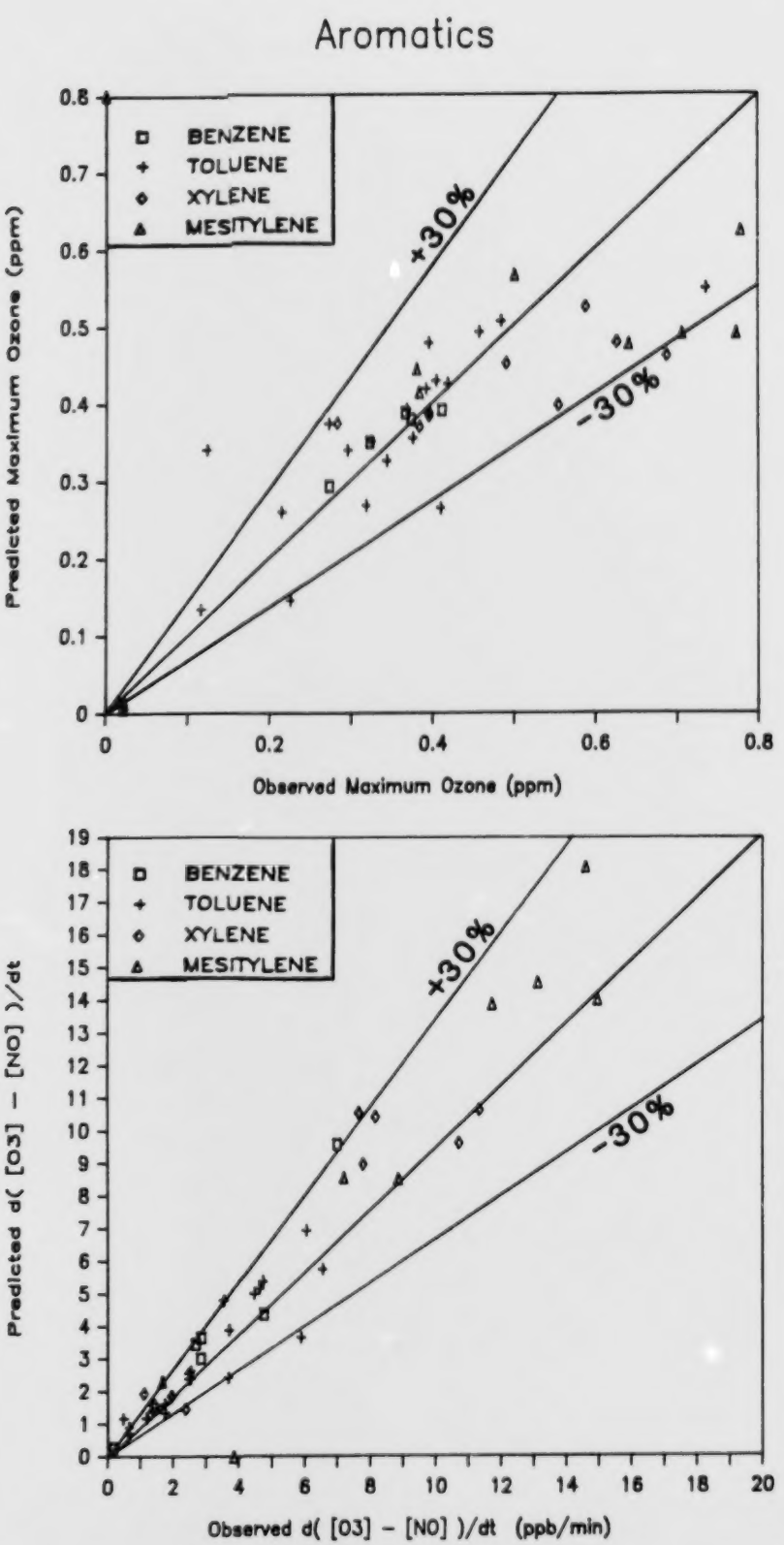


Figure 5. Predicted versus observed maximum ozone and $d([O_3]-[NO])/dt$ for aromatic-$NO_x$ runs

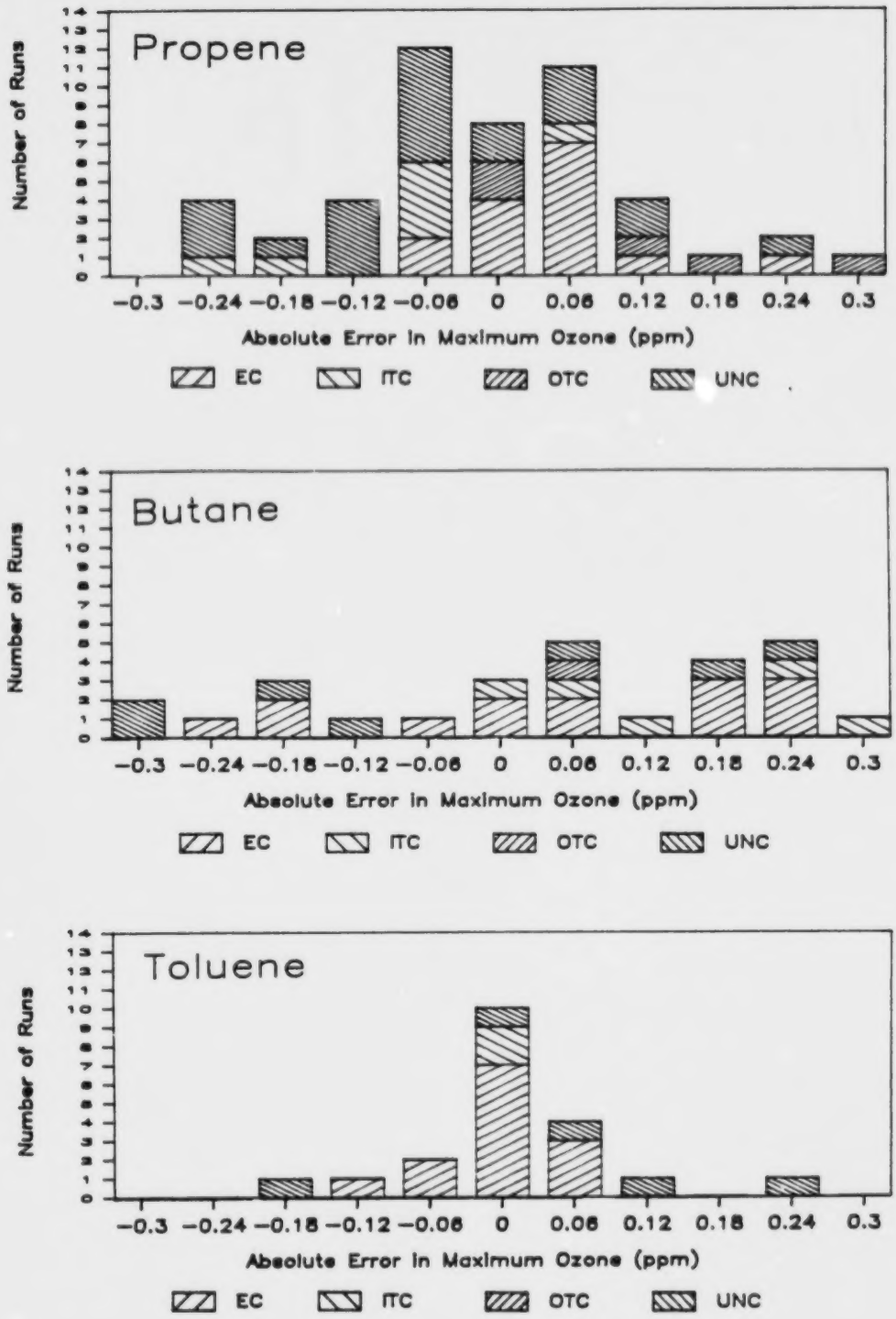


Figure 6. Distributions of absolute error in maximum ozone predictions for propene, n-butane, and toluene runs.

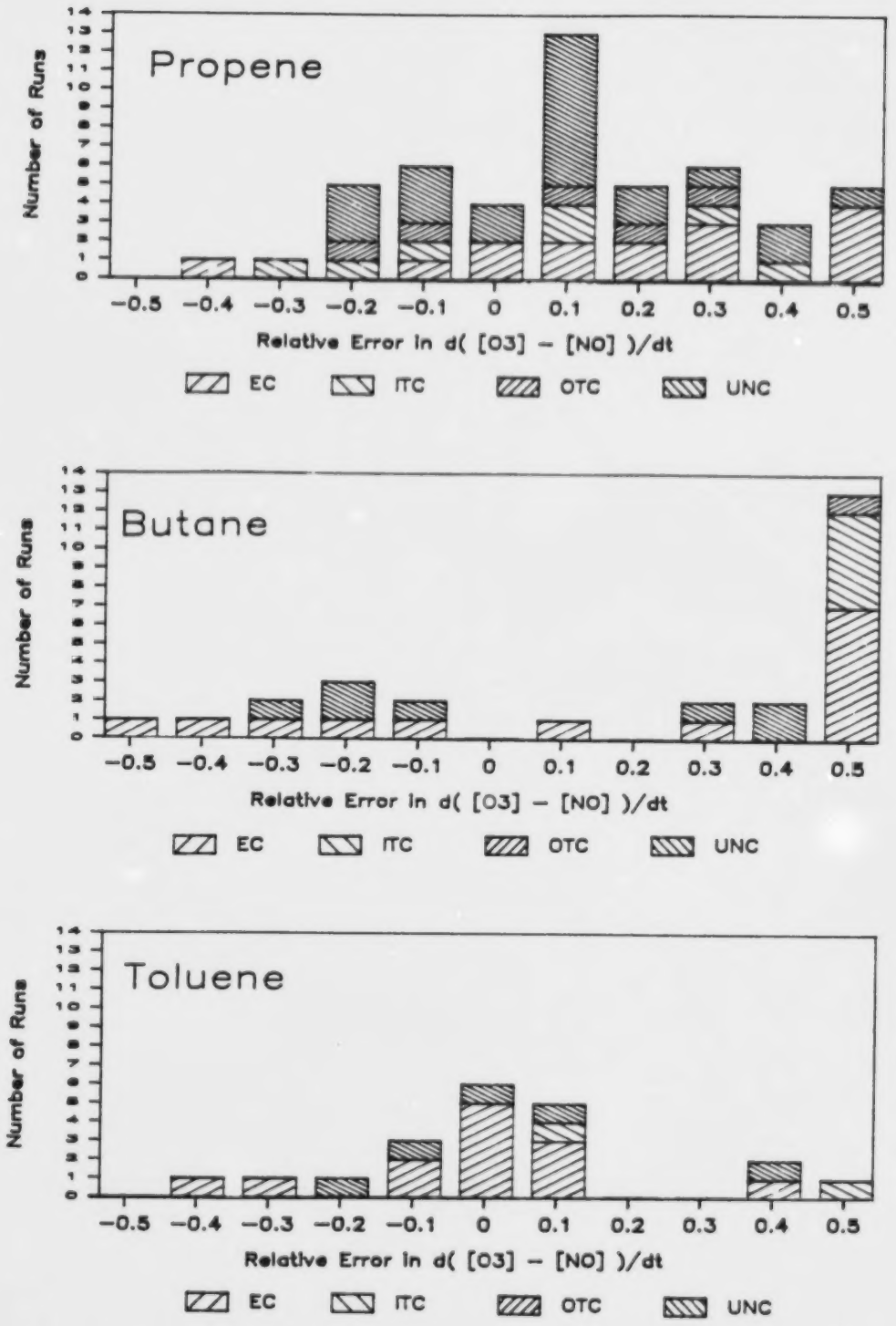


Figure 7. Distributions of relative errors in d([$O_3$]-[NO])/dt for propene, n-butane, and toluene runs.

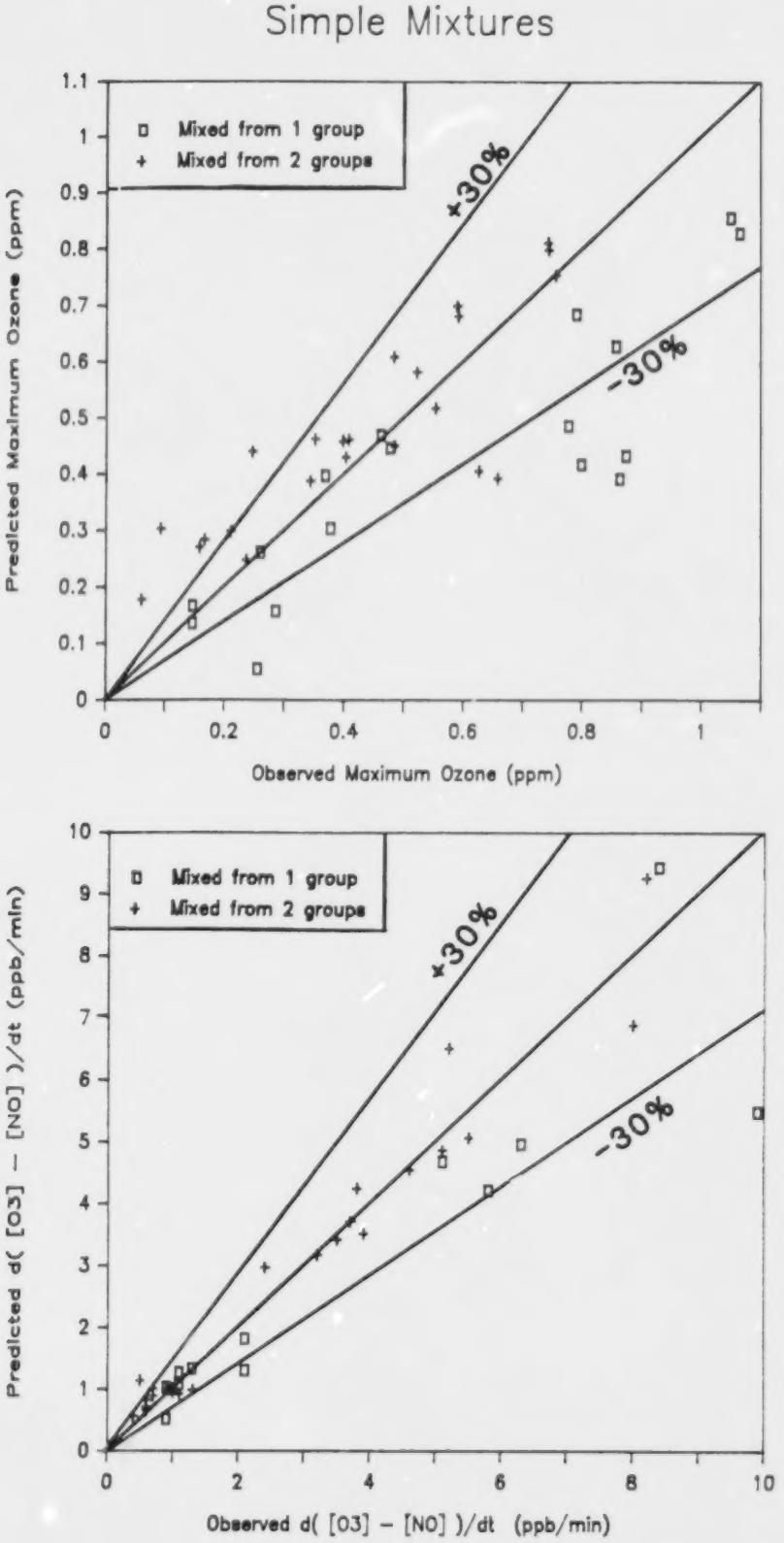


Figure 8. Predicted versus observed maximum ozone and $d([O_3]-[NO])/dt$ for simple organic mixture runs.

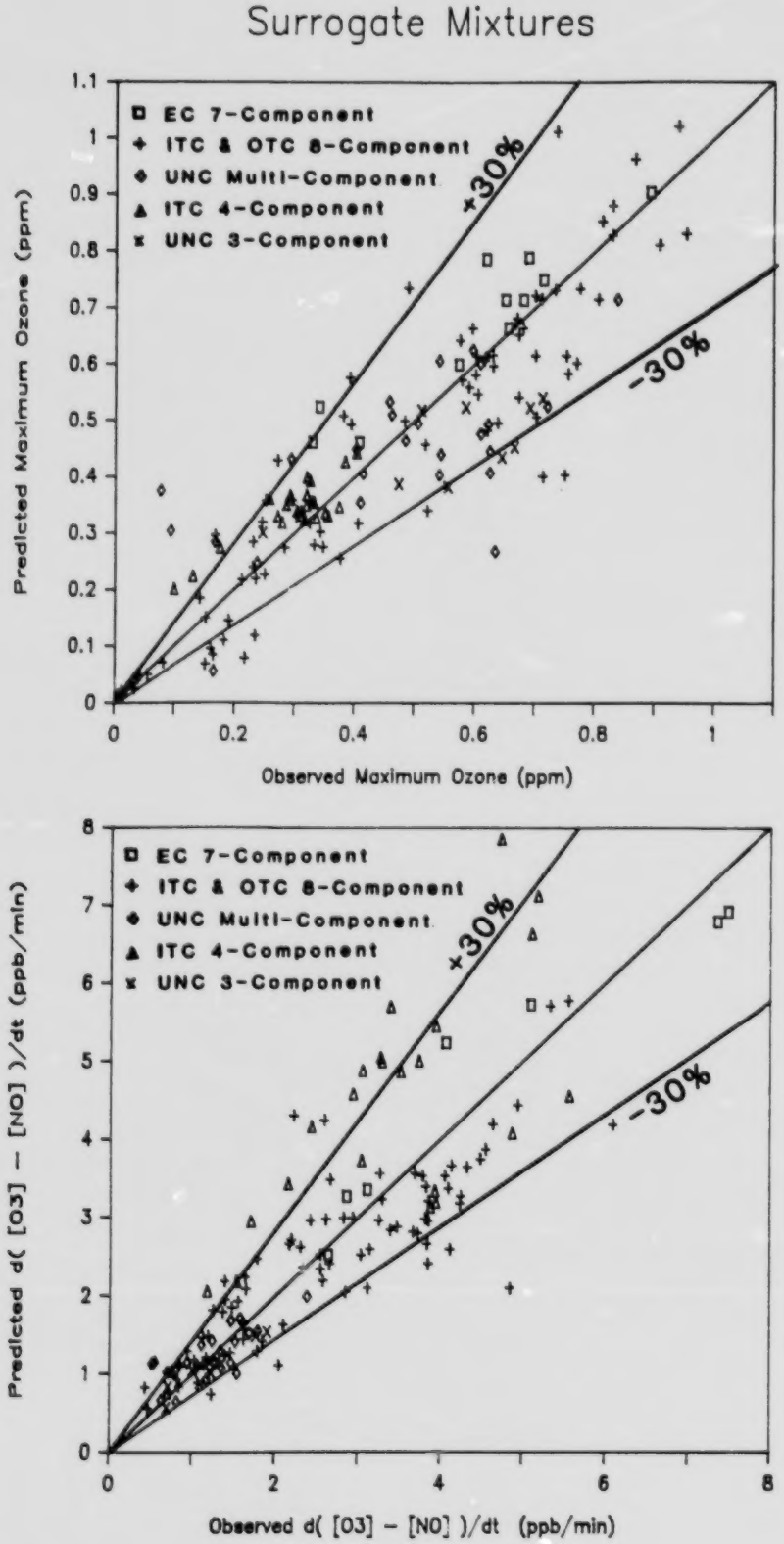


Figure 9. Predicted versus observed maximum ozone and $d([O_3]-[NO])/dt$ for surrogate mixture runs.

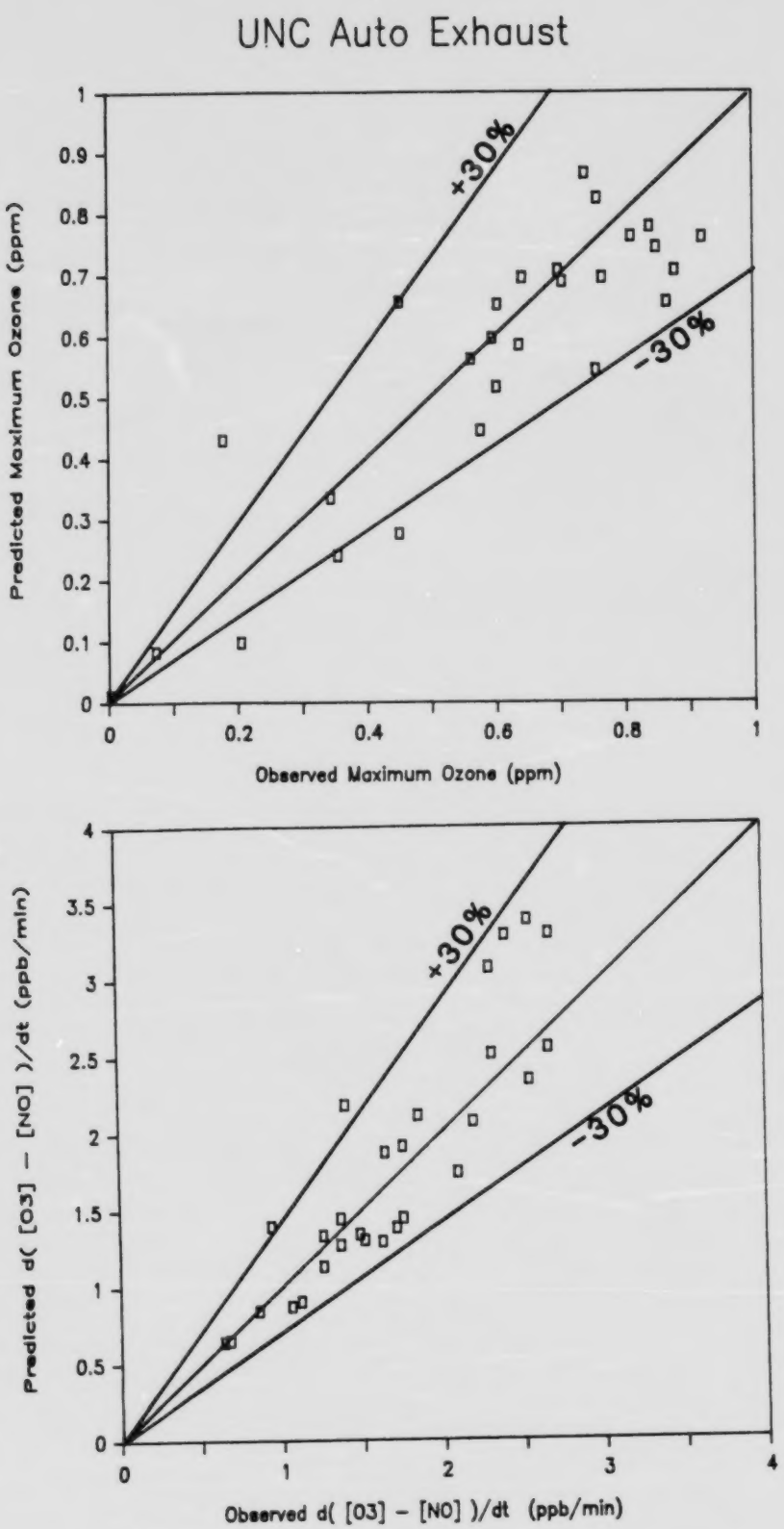


Figure 10. Predicted versus observed maximum ozone and $d([O_3]-[NO])/dt$ for UNC automobile exhaust runs.

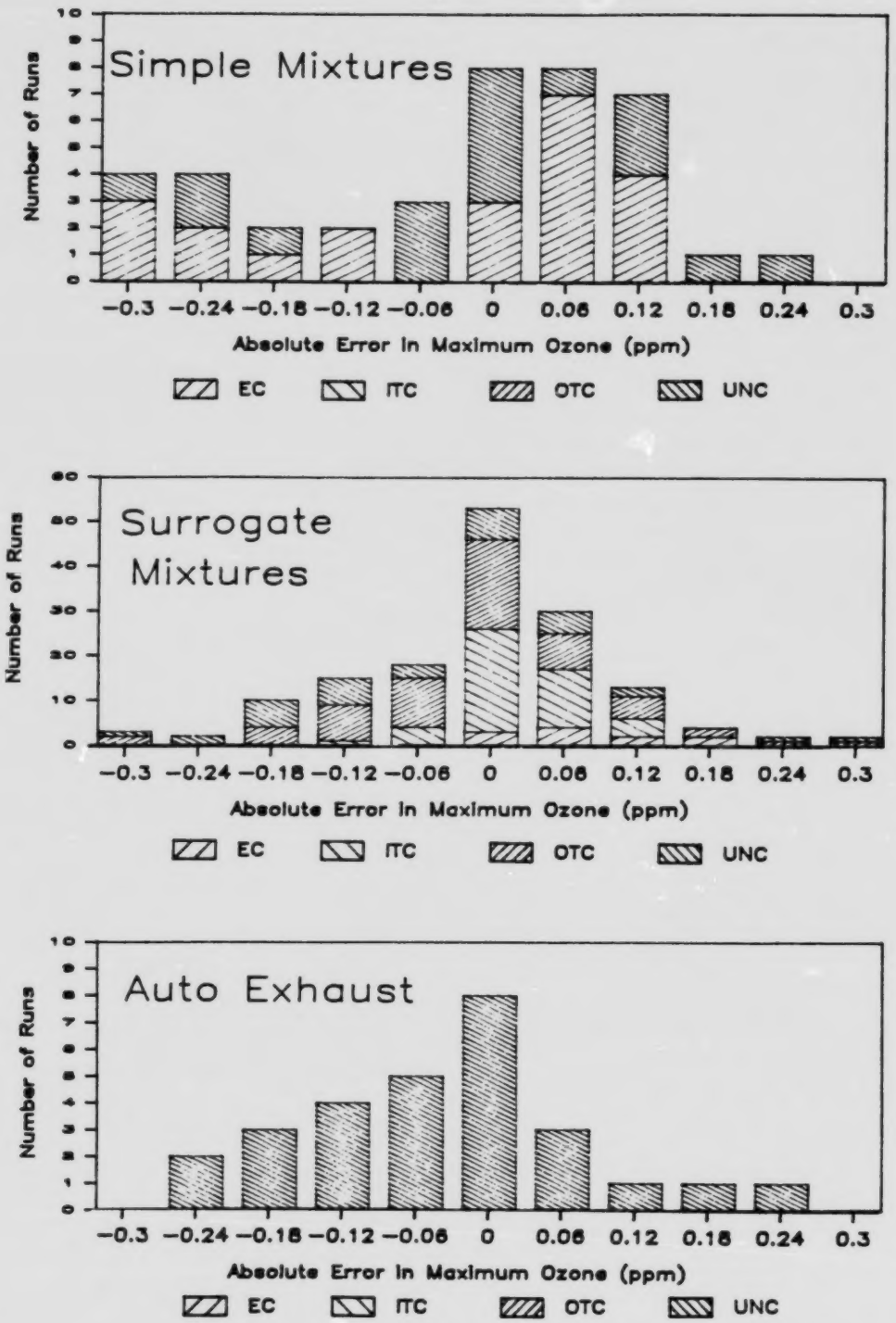


Figure 11. Distribution of absolute errors in maximum ozone predictions for simple mixtures, surrogate mixtures, and auto exhaust runs.

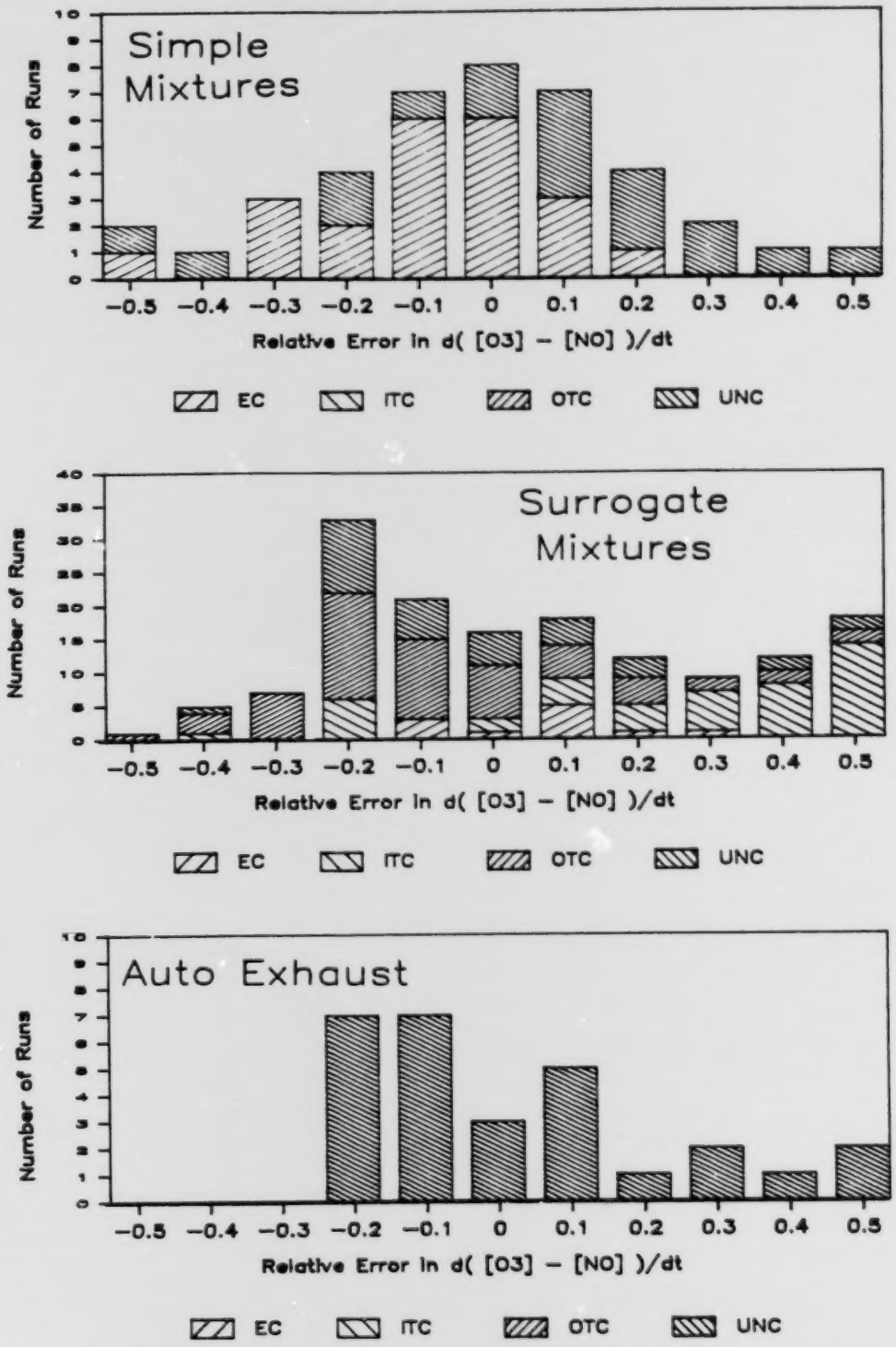


Figure 12. Distribution of relative errors in $d([O_3]-[NO])/dt$ for simple mixtures, surrogate mixtures, and auto exhaust runs.

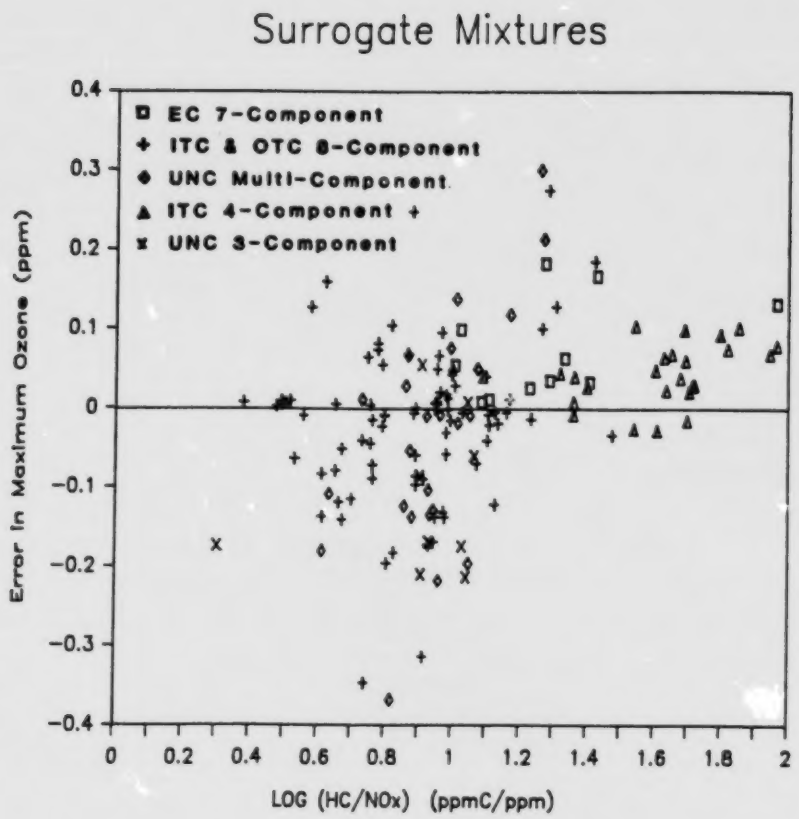


Figure 13. Absolute error in maximum ozone versus $\log_{10}$ ($NMOC/NO_x$)

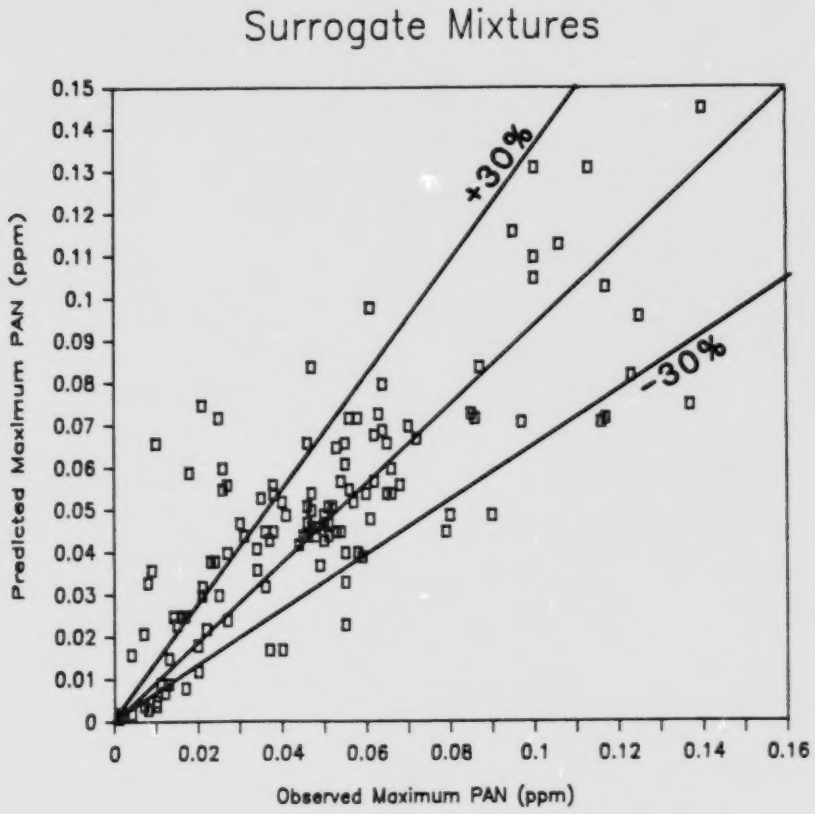


Figure 14. Predicted versus observed maximum PAN concentrations for surrogate mixture runs.

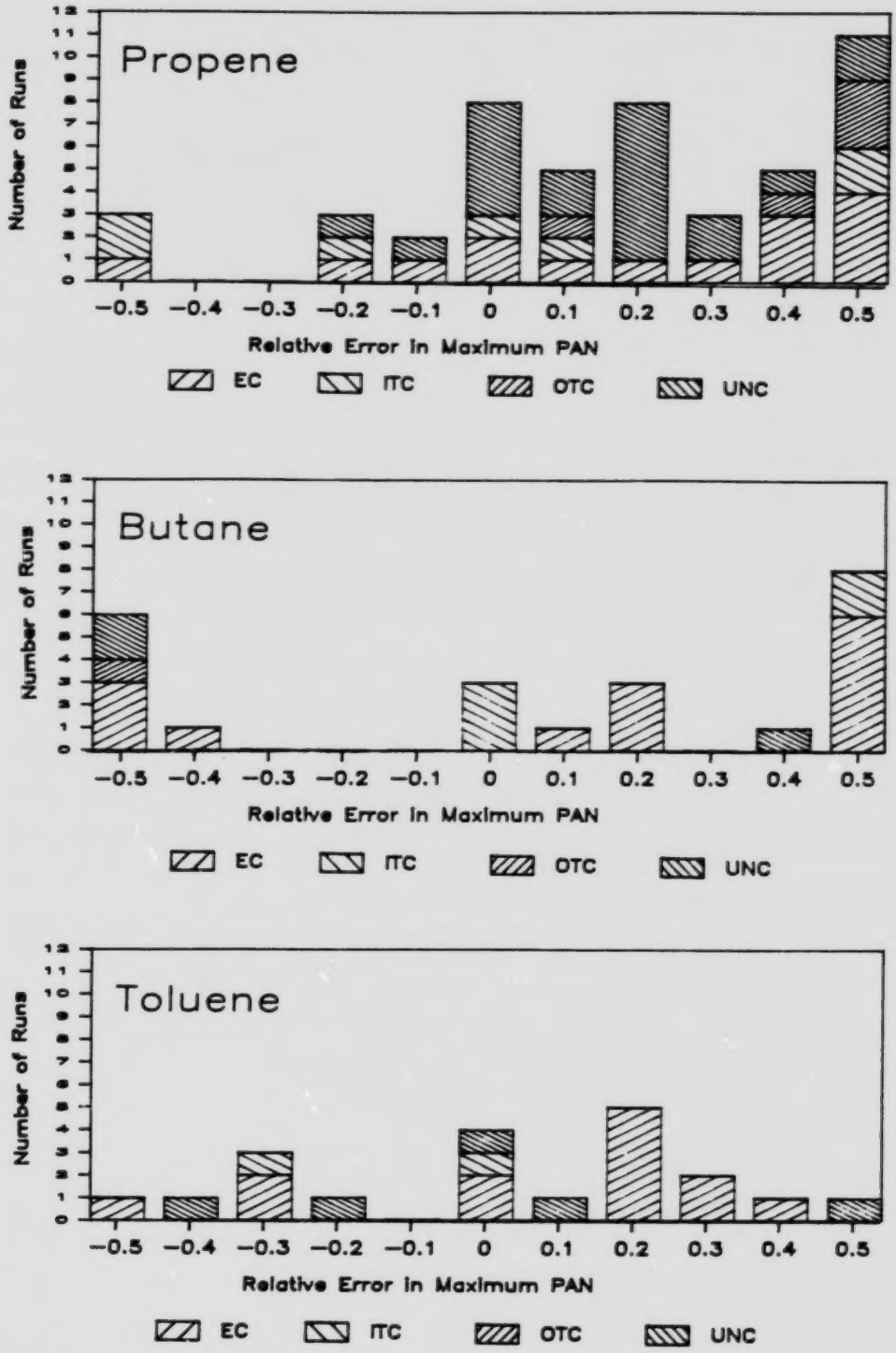


Figure 15. Distribution of relative errors in maximum PAN concentrations for propene, n-butane, and toluene runs.

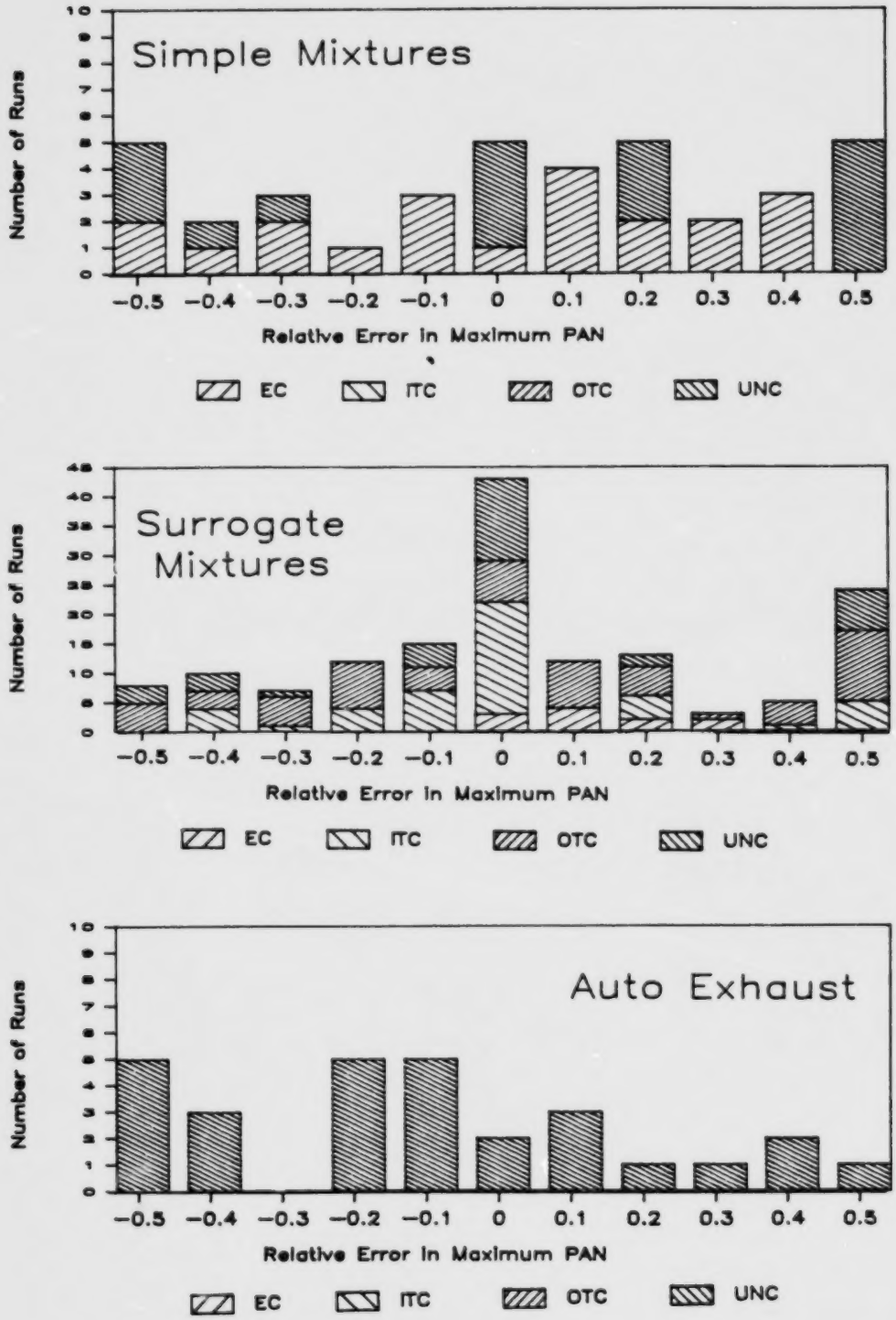


Figure 16. Distribution of relative errors in maximum PAN concentrations for simple mixture, surrogate mixture, and auto exhaust runs.

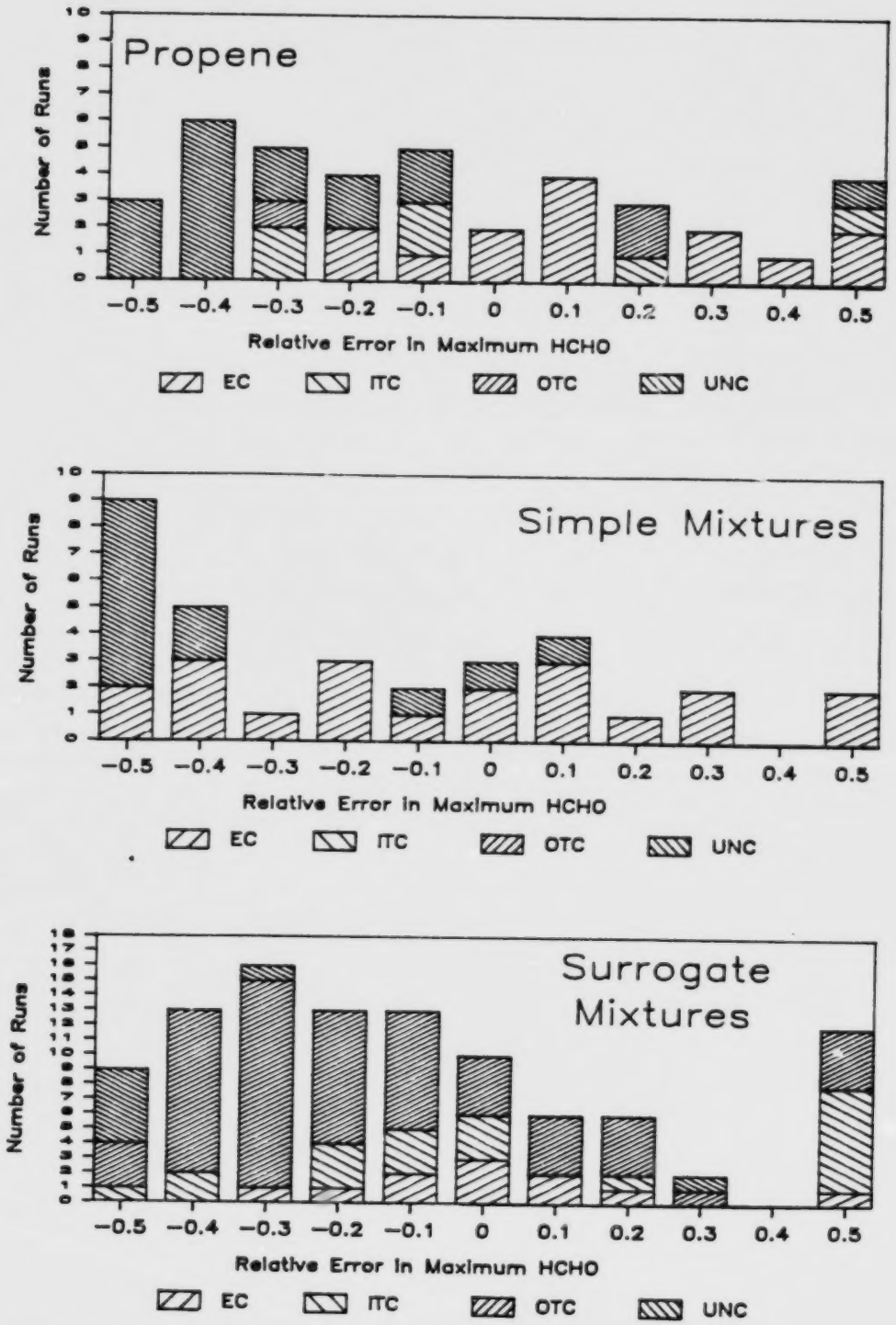


Figure 17. Distribution of relative errors in maximum formaldehyde concentrations for propene, simple mixture, and surrogate mixture runs.

# OZONE PRODUCTION IN RURAL AREAS

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## RÉSUMÉ

Une comparaison des mesures d'ozone prises dans divers sites ruraux de l'est et de l'ouest de l'Amérique du Nord indique que les valeurs quotidiennes maximales sont plus élevées dans l'est que dans l'ouest de 10 à 30 parties par milliard (ppb) et que les valeurs de plus de 80 ppb sont courantes dans l'est mais rares dans l'ouest. Le présent exposé a donc pour but de résumer les résultats d'une étude sur la climatologie des épisodes d'ozone dans l'est des États-Unis, tout en illustrant la fréquence, la durée et l'étendue spatiale des épisodes.

Lors de l'étude, un modèle simple de la couche limite a permis de réaliser une analyse photochimique de l'ozone des régions rurales américaines. Ce modèle tient compte de la croissance de la couche mixte durant le jour et de l'entraînement des espèces par le dessus. Les simulations ont été réalisées à partir des mécanismes chimiques de Lurmann, Lloyd et Atkinson (J. Geophys. Res., 91, 10905, 1986). En plus de la chimie de l'ozone, on a aussi examiné celle des espèces d'hydrogène et d'azote radicalaires pour un large éventail de concentrations de $NO_x$ et d'hydrocarbures. Les résultats montrent que les concentrations ambiantes de $NO_x$ et d'hydrocarbures dans les régions rurales de l'est des États-Unis sont suffisantes pour pousser les niveaux d'ozone à 80-100 ppb. Pour atteindre ces hauts niveaux d'ozone, trois conditions semblent essentielles: a) des températures chaudes, b) de l'air stagnant permettant aux concentrations d'ozone de s'accumuler sur une période de deux ou trois jours et c) des concentrations de $NO_x$ de 1,5-2 ppb ou plus durant

cette période de deux ou trois jours. La production d'ozone croît rapidement avec les niveaux de $NO_x$ jusqu'à ce que ceux-ci atteignent deux ou trois ppb; à des niveaux de $NO_x$ plus élevés, la production d'ozone peut diminuer sensiblement. La production d'ozone augmente également avec les concentrations d'hydrocarbures à condition que les concentrations de $NO_x$ soient de deux ppb ou plus. Enfin, les résultats du modèle sont comparables aux données sur l'air ambiant. En effet, les observations rurales montrent que les concentrations de $NO_x$ de deux ou trois ppb sont habituelles dans l'est des États-Unis, où les niveaux d'ozone sont élevés, mais rares dans l'ouest.

# OZONE PRODUCTION IN RURAL AREAS

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A comparison of ozone measurements from rural sites in eastern and western North America indicates that daily maximum values are 10-30 ppb higher in the east than the west, and that high values (>80 ppb) are common in the east and rare in the west. We will summarize results of a study of the climatology of ozone episodes in the eastern U.S., illustrating the frequency, duration and spatial extent of the episodes.

A simple boundary layer model was used to investigate the photochemistry of ozone in rural areas of the U.S. The model allows for growth of the mixed layer during the day and entrainment of species from above. Simulations employed the chemical mechanism of Lurmann, Lloyd and Atkinson (J. Geophys. Res., 91, 10905, 1986). We examined the chemistry of ozone, odd-hydrogen and odd-nitrogen species for a wide range of $NO_x$ and hydrocarbon concentrations. Results show that ambient concentrations of $NO_x$ and hydrocarbons in rural areas of the eastern U.S. are sufficient to cause ozone levels to reach 80-100 ppb. Elevated ozone levels appear to require three conditions: (a) warm temperatures; (b) stagnant air that allows ozone concentrations to build up over 2-3 days; and (c) $NO_x$ levels of 1.5-2 ppb or higher throughout the 2-3 day period. Ozone production is found to increase sharply with $NO_x$ levels until $NO_x$ reaches 2-3 ppb; for higher $NO_x$ levels ozone productions may decrease slightly. Ozone production increases with hydrocarbon concentration only for $NO_x$ levels of 2 ppb or higher. Model results compare favorably with ambient air data. Rural observations show that $NO_x$ levels of 2-3 ppb are common in the eastern U.S., where elevated ozone levels are observed, but rare in the western U.S.

# CHEMICAL CONSIDERATIONS IN CALIFORNIA'S OZONE CONTROL STRATEGY

(Text not provided)

Dr. John R. Holmes
Research Division
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# OXIDANTS FOR ATMOSPHERIC SULFUR (IV)

Dr Gregory L. Kok
National Center for Atmospheric Research
Boulder

## RÉSUMÉ

Les trois principaux oxydants de l'anhydride sulfureux ($SO_2$) dans l'atmosphère sont l'hydroxyle (OH), l'ozone ($O_3$) et le peroxyde d'hydrogène ($H_2O_2$). L'hydroxyle contribue à l'oxydation en phase gazeuse du $SO_2$, tandis que l'$O_3$ et le $H_2O_2$ interviennent dans la phase aqueuse. Des calculs effectués à partir d'un modèle démontrent que près de la moitié du $SO_2$ est oxydée en phase gazeuse et que l'autre moitié l'est en phase aqueuse. Des mesures récentes du $H_2O_2$ dans l'est des États-Unis indiquent que le peroxyde peut être un oxydant majeur du $SO_2$. Elles montrent aussi que les concentrations du peroxyde d'hydrogène dans la couche limite sont beaucoup plus basses que celles dans la trophosphère libre. La quantité nette de $H_2O_2$ assimilée par les nuages et disponible pour l'oxydation du $SO_2$ varie fortement en fonction de la dynamique atmosphérique à proximité des nuages.

## ABSTRACT

The three major oxidants for sulfur dioxide ($SO_2$) in the atmosphere are hydroxyl radicals (OH), ozone ($O_3$) and hydrogen peroxide ($H_2O_2$). Hydroxyl radicals contribute to the gas-phase oxidation of $SO_2$ where $O_3$ and $H_2O_2$ are effective only in the aqueous-phase. Model calculations demonstrate that approximately half of the $SO_2$ is oxidized in the gas phase and the remainder in the aqueous phase. Recent measurements of $H_2O_2$ in the Eastern United States indicate that it can be a major oxidant for $SO_2$. These studies show that hydrogen peroxide concentrations in the boundary layer are significantly lower than those in the free troposphere. The net amount of $H_2O_2$ which will be taken up into clouds and be available for the oxidation of $SO_2$ will be a strong function of the atmospheric dynamics near clouds.

The formation of the sulfate species is controlled by the abundance of atmospheric oxidants which can convert $SO_2$ to sulfate. The oxidation of $SO_2$ takes place both in the gas phase and in the aqueous phase(cloud or fog droplets). For the gas-phase oxidation of $SO_2$ the most significant oxidant is the hydroxyl radical (OH) (Stockwell and Calvert, 1983; Margitan, 1984). Other radical species such as hydroperoxyl($HO_2$) and methylhydroperoxyl($CH_3OO$) are not significant contributors to the gas-phase oxidation. (Burrows *et al.*, 1979; Graham *et al.*, 1979; Cocks *et al.*, 1986). In the aqueous phase, two oxidants, hydrogen peroxide and ozone, have sufficient atmospheric abundance and rapid reaction kinetics to be the major oxidants. (Penkett *et al.*, 1979; Martin and Damschen, 1981; Kunen *et al.*, 1983; Maahs, 1984). The reaction rate constants of these oxidants with $SO_2$ are strongly pH dependent. For ozone the reaction rate constant with $SO_2$ decreases as the pH decreases. The opposite is true for $H_2O_2$ as the reaction rate with $SO_2$ increases as the pH decreases between pH 6 and 2. Combining both the solubility of the oxidants and $SO_2$ with the kinetic rate constant as a function of pH shows that oxidation by $H_2O_2$ is pH invariant over the range 2-7 and that the oxidation by $O_3$ drops by nearly two orders of magnitude per pH unit as the pH decreases over the range 2-7. Based on estimated atmospheric abundances of $H_2O_2$ and $O_3$ the crossover point is approximately pH 4.5. At pH values above 4.5 oxidation by $O_3$ dominates where as $H_2O_2$ is the dominant oxidant below this pH. A detailed discussion of the relative importance of several aqueous oxidants for $SO_2$ is given by Calvert *et al.* (1985).

The mechanism by which $SO_2$ is oxidized to sulfate is critically dependent on the availability of oxidants and meterological conditions. For example, if $SO_2$ is emitted into a cloud-free atmosphere at night, it will have no significant mechanism available for oxidation and it will be removed only by dry deposition. Under these conditions $SO_2$ can be transported considerable distances and will be deposited over a wide area. An even wider distribution of sulfur deposition will occur if $SO_2$ is emitted during daylight hours into cloud-free conditions, since OH will oxidize $SO_2$ to sulfate and this has a slower deposition velocity than $SO_2$ (Walcek *et al.*, 1986).

Considering the emission of $SO_2$ into conditions where clouds are present and precipitation is imminent, $SO_2$ has the potential to be deposited in a region near the emission source. For this to occur there must be sufficient aqueous oxidant present to

convert the $SO_2$ to sulfate. If there is insufficient oxidant, the $SO_2$ will be transported longer distances before deposition.

The above considerations of oxidant availability relate to source-receptor relationships and control strategies. Since the pH of most precipitation falls below 4.5 the dominant aqueous oxidant is $H_2O_2$. If sufficient $H_2O_2$ is available to oxidize $SO_2$ the probability for near-source deposition of sulfur is enhanced, therefore control measures instituted on a source will benefit the local region in a direct source-receptor relationship. If insufficient $H_2O_2$ is available the source-receptor relationship is spread out over a larger area.

*Generation of Oxidants.*

Predicted concentrations of oxidants generated by the photochemistry of the atmosphere are derived through the use of photochemical models. Many models have been formulated to describe the photochemical production of oxidant generation and subsequent transformation of sulfur species (Stockwell, 1986). A discussion of the photochemistry of the global troposphere has been presented by Logan *et al.*, (1981). The following summarizes the atmospheric chemistry leading to the formation of OH and $H_2O_2$ in the atmosphere. The production of OH and $H_2O_2$ begins with the photolysis of $O_3$ to yield excited state oxygen atoms.

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad (1)$$

The next step is the formation of OH radicals.

$$O(^1D) + H_2O \rightarrow OH + OH \qquad (2)$$

The OH radicals produced react with $SO_2$ to produce sulfate species

$$OH + SO_2 \rightarrow \text{sulfate} + HO_2 \qquad (3)$$

The production of $H_2O_2$ in the atmosphere is through the combination of hydroperoxyl radicals, $HO_2$.

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (4)$$

Reaction of OH with CO produces H atoms, which go on to form $HO_2$.

$$OH + CO \rightarrow H + CO_2 \qquad (5a)$$

$$H + O_2 \rightarrow HO_2 \qquad (5b)$$

Photolysis of formaldehyde (HCHO) will also generate two $HO_2$ radicals through a multistep process. The net reaction is given in equation 6.

$$HCHO + h\nu + 2O_2 \rightarrow 2HO_2 + CO \qquad (6)$$

The production of $HO_2$ by reaction (5) is approximately an order of magnitude greater than that given by reaction (6) for conditions typical of the Eastern United States (Walcek, 1987).

The production of $O_3$ is significantly dependent on the nature and age of the hydrocarbons and nitrogen oxides present. This is addressed extensively in other papers presented in this symposium and will not be detailed here.

The production of these oxidants is driven by photolytic processes and therefore at sunset the production process stops. The concentration of hydroxyl radical becomes negligible and its reaction with $SO_2$ will stop. The lifetimes of $O_3$ and $H_2O_2$ are much longer and they can react with $SO_2$ at night in clouds or on wet aerosol particles.

*Oxidant Availability*

The amount of oxidation of $SO_2$ that takes place in the gas phase is impossible to quantitate experimentally. Gas-phase measurements of $SO_2$ can be made with good accuracy. However, present technology is inadequate to measure the concentration of OH radicals in the atmosphere. To bridge this measurement gap, detailed models of the photochemistry of the atmosphere have been developed (Calvert *et al.*, 1985; Stockwell, 1986; Whitten *et al.*, 1980). These models indicate that approximately half of the $SO_2$ oxidized in the atmosphere is through the gas-phase pathway. Until quantative measurements of OH radicals are made it will be difficult to accurately predict the total amount of $SO_2$ oxidized in this pathway.

The aqueous-phase oxidation of $SO_2$ is controlled by $O_3$ and $H_2O_2$. Since most cloud water and precipitation is below pH 4.5, $H_2O_2$ is the dominant oxidant. The recent development of the enzyme-based fluorometric analytical technique for the determination of $H_2O_2$ in both the aqueous phase and gas phase has opened up the potential to quantitate the importance of $H_2O_2$ as an oxidant for $SO_2$ (Lazrus *et al.*, 1985; Lazrus *et al.*, 1986).

Measurement programs to determine the atmospheric abundance of $H_2O_2$ have concentrated on the Eastern United States with measurements being made in cloud water impacting Whiteface Mountain (Lazrus *et al.*, 1987), stratiform clouds (Daum *et al.*, 1984; Kelly *et al.*, 1985) and the gas-phase (Heikes *et al.*, 1987). These studies confirm the importance of $H_2O_2$ as an oxidant for $SO_2$ in the aqueous phase.

The largest body of data on atmospheric $H_2O_2$ concentrations has been collected at Whiteface Mountain, New York (Lazrus *et al.*, 1987). $H_2O_2$ has been measured in cloudwater from 1982 through the present time. Samples were collected from nonprecipitating clouds, including both warm clouds and supercooled clouds. A strong diurnal variation is observed. During the winter months, the concentration of $H_2O_2$ in the cloud water was extremely low, less than $1 \times 10^{-8}$ M. The highest values of $H_2O_2$ are measured in June with a median concentration of 22 micromolar and a number of samples containing in excess of 100 micromolar.

The data from stratiform clouds provides considerable information on the relationship between $H_2O_2$, $O_3$ and $SO_2$ (Daum *et al.*, 1984; Kelly *et al.*, 1985). These studies showed that the peroxide concentrations in cloud water ranged from 0.1 to over 100 uM with the median values less than 10 uM. The highest concentrations were observed in summer. There was an anticorrelation between gas-phase $SO_2$ and $H_2O_2$ concentrations in cloud water, indicating that the $SO_2$ is being taken up in the cloud water and reacting with the $H_2O_2$.

A more recent series of measurements have been made studying the gas-phase concentrations of $H_2O_2$, $O_3$ and $SO_2$ in the Eastern United States (Heikes *et al.*, 1987). A total of 29 sampling profiles were made with the vertical distribution of these species measured from ground level to 3.5 km. The measurements were made in October and

early November of 1984. All measurements were made in clear air and generally under conditions of southerly air flow.

Detailed analysis of the data is given by Heikes *et al.*, (1987). Figure 1 shows a selected profile from this data set. Sampling was conducted near VanWert, Ohio on October 16, 1984. The area had been under the influence of southerly air flow for the two preceding days. There was a thin cloud layer present from about 0.9-1.1 km. An examination of the $SO_2$, $H_2O_2$, relative humidity and specific humidity (Q) shows two composition regions separated by the cloud layer. The highest $SO_2$ and the lowest $H_2O_2$ concentrations are measured below cloud in the boundary layer. Above the cloud layer the $SO_2$ conctrations drops and the $H_2O_2$ concentration increases. The ozone concentration does not markedly change with altitude.

The profile in figure 1 is typical of that measured in this sampling program (Heikes *et al.*, 1987). Considering the anticorrelation between $SO_2$ and $H_2O_2$ it is difficult to directly analyze the availability of $H_2O_2$ for in-cloud oxidation of $SO_2$. In the boundary layer there is a deficiency of $H_2O_2$, while above the boundary layer $H_2O_2$ is typically in excess of $SO_2$. The net concentrations of these species in cloud water will depend on the amount of air from the boundary layer containing $SO_2$ mixed with $H_2O_2$-rich air from above. This mixing will depend on cloud type as well as other variables and more research is needed.

*Summary*

The picture with regard to the availability of oxidants for $SO_2$ in the atmosphere is becoming clearer as as analytical techniques and computer models improve. In summer increased photolytic activity raises the OH concentrations as well as those of the other oxidants $H_2O_2$ and $O_3$. Computer models of OH oxidation of $SO_2$ and gas and aqueous-phase measurements of $H_2O_2$ suggest that the oxidants are present in adequate quantities to promote the rapid oxidation of $SO_2$. In winter the oxidation by OH drops by nearly an order of magnitude (Calvert *et al.*, 1985) and the measured concentration of $H_2O_2$ is reduced over two orders of magnitude (Lazrus *et al.*, 1987). Both of these factors significantly reduce the oxidant potential for $SO_2$. Under these circumstances the dry deposition of $SO_2$ will be increased and $SO_2$ will be transported a greater distance before it is oxidized to sulfate and deposited.

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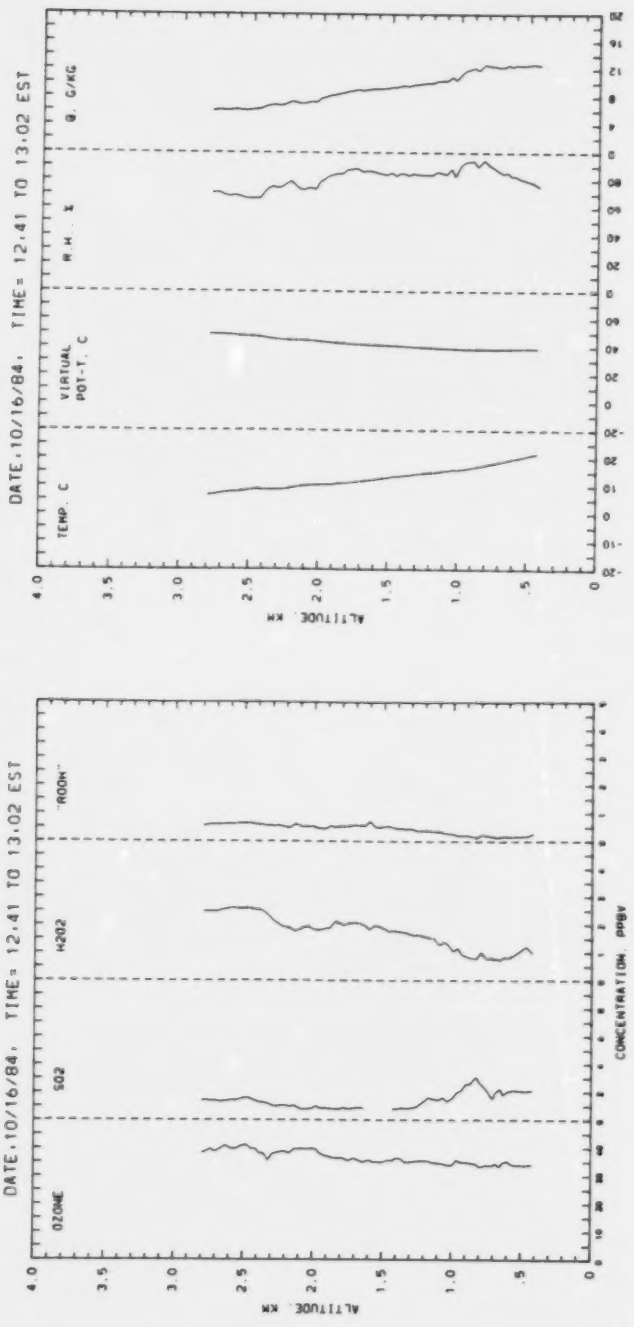


Fig. 1 Vertical profile of $O_3$, $SO_2$, $H_2O_2$, "ROOH" and meteorological information measured near Van Wert, Ohio, on October 16, 1984.

# IMPACT OF NATURAL HYDROCARBONS ON RURAL OZONE: MODELING AND OBSERVATIONS

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Estimates show that the emission rate of natural hydrocarbons, like isoprene and mono terpenes, can be as large or larger than the emission rate of anthropogenic hydrocarbons. A study by Lamb et al. (1987) shows that in the United States 63% of the total nonmethane hydrocarbon (NMHC) emissions are of natural and 37% of anthropogenic origin. Since natural hydrocarbons are more reactive than most of the anthropogenic NMHCs, a large impact of the natural NMHCs on the photochemistry of the rural atmosphere can be expected.

However, previous studies of the importance of natural NMHCs for the formation of ozone in the rural troposphere gave inconclusive results, with the general conclusion that their impact is small (Altshuller, 1983; Lurmann et al., 1983, 1984). But, uncertainty in the emission rates of natural hydrocarbons and the lack of simultaneous measurements of key photochemical species has prevented a definitive evaluation.

Recently, Lamb et al. (1985, 1987) made an extensive evaluation of the natural NMHC emission flux. They showed that consistent estimates of the biogenic emission of isoprene can be obtained by three independent measurement methods. In addition, during the summer 1986, concentrations of key trace gases were measured at Scotia, Pennsylvania, a rural site in the eastern United States. These measurements enable a realistic case study of the impact of natural NMHC on the photochemistry and ozone formation in rural air.

In the following, a high resolution 1-dimensional planetary boundary layer (PBL) model that includes isoprene photochemistry (Trainer et al., 1987) will be used to evaluate the effect of natural NMHC on the formation of rural ozone.

Measurements

During the summer of 1986, a comprehensive field experiment was carried out at Scotia, Pennsylvania to study the photochemistry of rural ozone and acid deposition. The site is located in a forest preserve 10 km west of State College, PA and is removed from any direct anthropogenic emission source. Furthermore, the site is a monitoring station of the National Acid Precipitaion Assessment Program (NAPAP) with well characterized meteorology. The trace gases measured at the site include NO, $NO_2$, $HNO_3$, $NO_y$ which is the sum of the reactive nitrogen species (Fahey et al., 1986), $O_3$, $NO_3^-$, and $SO_4^=$, PAN , individual NMHC up to $C_{10}$, including the natural NMHC, $CH_2O$ and $CH_3CHO$.

Ozone shows a characteristic diurnal cycle at the site (Fig. 1). At night, $O_3$ is suppressed due to surface deposition in a shallow inversion layer. In the morning hours, $O_3$ increases during the breakup of the nocturnal inversion layer when air from aloft is mixed downward. During the daytime, $O_3$ increases due to photochemical formation. The highest $O_3$ concentrations at the site are observed under high pressure conditions, with low surface winds, high temperatures and predominantely clear skies. Under stagnant high pressure systems that persist for several days and allow the accumulation of precursors and secondary products, high $O_3$ concentrations are frequently observed over large regional scales (Vukovich et al., 1977; Guicherit and van Dop, 1977). For the model calculations a 4 day period is chosen to provide the model parameters. During the period from 4 July through 7 July 1986, Central Pennsylvania was at the northern edge of a stagnant high pressure system over the Eastern U.S. The peak $O_3$ concentration observed during this 4-day period at Scotia reached over 110 ppbv, close to the national ambient $O_3$ standard.

The daytime average hydrocarbon mixing ratios observed at the site during this period are shown in Fig. 2. The horizontal bars indicate the times during which several individual hydrocarbon samples were collected. During these 4 days, the natural NMHC isoprene is the predominant hydrocarbon at the site. The vertical bars indicate its variation throughout the day. Isoprene concentrations were low in the morning hours and increased throughout the day as the temperature increased. Furthermore, the average isoprene concentration increased during the 4 day period as the average daytime temperature increased.

Model Calculations

In the model calculations, the temperature dependence of the isoprene emission rate is described according to measurements by Lamb et al. (1985) at a forest site in Eastern Pennsylvania. For the height at which the samples were taken (i.e. 5m) the maximum isoprene concentration predicted by the model is 5 ppbv or 15 $\mu g\ m^{-3}$, which is well within the range of the observed values.

The observed anthropogenic hydrocarbons are mainly alkanes, while the more reactive olefins of anthropogenic origin are strongly depleted during this stagnant period. For this reason we have scaled the emission rates of the anthropogenic NMHC to the $NO_x$ emissions with scaling factors of .3 for propane and butane and .075 for ethyene and propene.

The emission rate for $NO_x$ is chosen to reproduce the observed diurnal pattern of $NO_x$. During the 4 day period, $NO_x$ showed a sharp peak in the morning which coincided with the breakup of the nocturnal inversion layer and which lasted for 1 to 2 hours (Fig. 3). The $NO_x$ concentrations during the daytime were around 1 ppbv. Since there is no appreciable local $NO_x$ source, the $NO_x$ is probably transported to the

site from distant sources. In order to simulate this phenomenon (Fig. 4) a continuous $NO_x$ emission rate is assumed for the height range from 200 to 800 m. During the night time the vertical mixing is slow and $NO_x$ accumulates in this emission layer. The surface, where the measurements are taken is isolated from the air aloft during the night by the shallow inversion layer. In the morning, when the inversion breaks up, downward mixing of $NO_x$ leads to the sharp early morning rise. The subsequent decline is due to dilution as the PBL height increases during the daytime and due to photochemical conversion of $NO_x$ to PAN and $HNO_3$. The rate of the $NO_x$ emission, chosen to reproduce the observed diurnal variation, is $4 \times 10^{15}$ $m^{-2} s^{-1}$. This value agrees with the average $NO_x$ emission rate in Western Pennsylvania as derived from the NAPAP emission estimates.

Results

Figure 5 shows the predicted ozone variation for a 4 day period at a height of 5 m for this $NO_x$ emission rate and various hydrocarbon scenarios. If no hydrocarbons are emitted and only CO and $CH_4$ oxidation are considered, the daytime maximum ozone values are approximately 55 ppbv. If isoprene emission is included, a strong buildup of ozone during the 4 day period is predicted. Additional inclusion of the emission of anthropogenic hydrocarbons shows only a small additional increase in the ozone production. The system is in a strongly nonlinear regime where an increase of the hydrocarbon emission rate does not lead to a corresponding increase in the ozone production rate. Ozone formation, under these conditions, is $NO_x$ limited. We have made a calculation that includes first the emission of anthropogenic NMHCs and then the addition of isoprene. In this case most of the ozone increase (about 65%) is due to anthropogenic NMHCs. Many previous studies that considered only this scenario may have therefore underestimated the contribution of isoprene to rural ozone formation.

The maximum $O_3$ concentrations observed at the site show values close to the national ambient ozone standard of 120 ppbv (Fig. 6). The model that includes the hydrocarbon emissions simulates the observed peak ozone concentrations well except for 7 July. The decline in $O_3$ observed on 7 July may indicate an approaching cold front and change of air masses at the site. This effect still has to be studied in more detail.

The comparison of model prediction and observation indicates that the oxidation of $NO_x$, which is mainly of anthropogenic origin, in the presence of naturally emitted isoprene, at levels observed at this rural site, can lead to high ozone concentrations during a stagnant high pressure period.

## Conclusions

For conditions observed at Scotia, a rural site in Central Pennsylvania, anthropogenic $NO_x$ in combination with natural isoprene, leads to most of the ozone production. A reduction of the emission of anthropogenic hydrocarbons will not substantially reduce the ozone formation in rural air. If high ozone in rural ares is of concern, consideration has to be given to a reduction of the anthropogenic $NO_x$ emissions.

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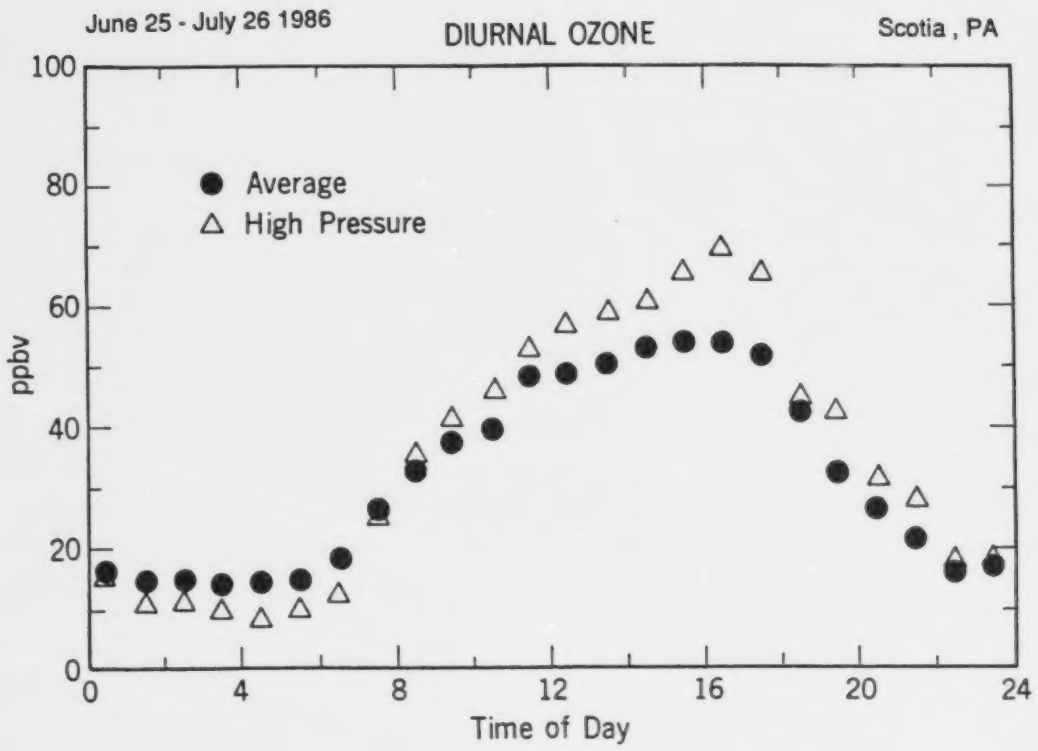


Figure 1 :
The average diurnal ozone mixing ratio at Scotia, PA for June 25 - July 26 1986 (circles) and for times when the surface pressure was larger than the average pressure of 970 mb (triangles).

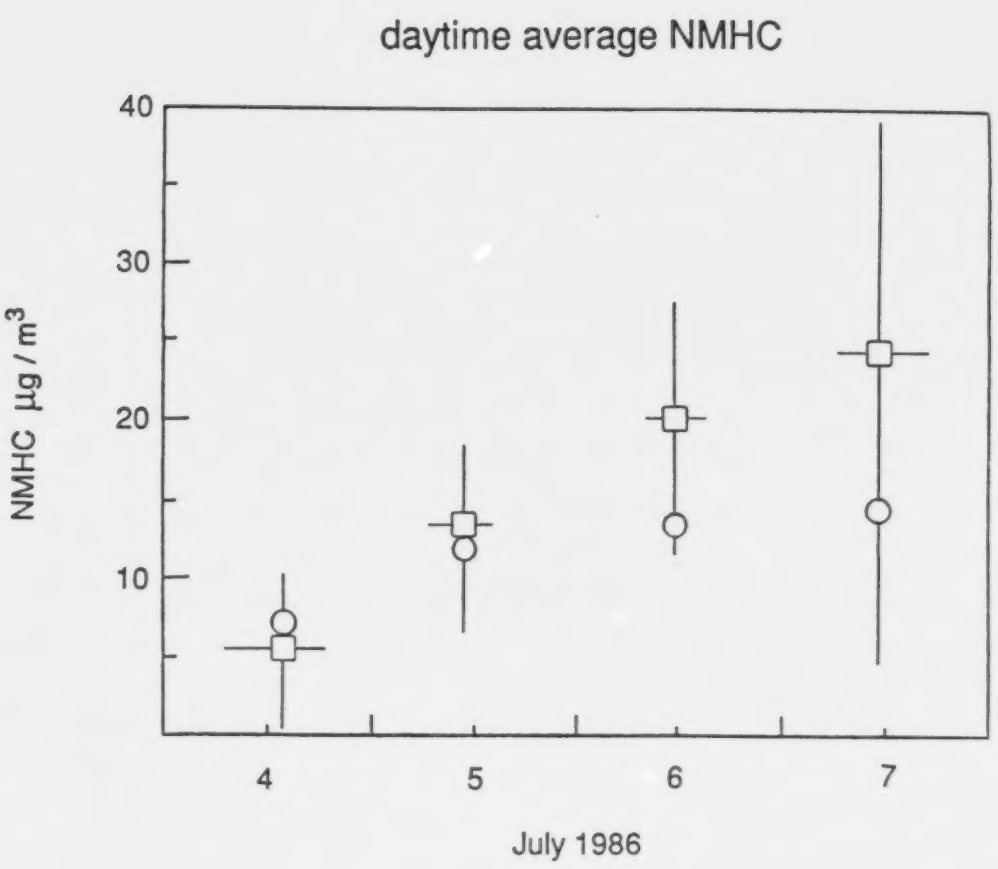


Figure 2 :
The average isoprene (squares) and anthropogenic NMHC (circles) mixing ratios at Scotia, PA for July 4 - July 7 1986. The horizontal bars indicate the times during which several individual samples were taken. The vertical bars indicate the variation of isoprene throughout the day.

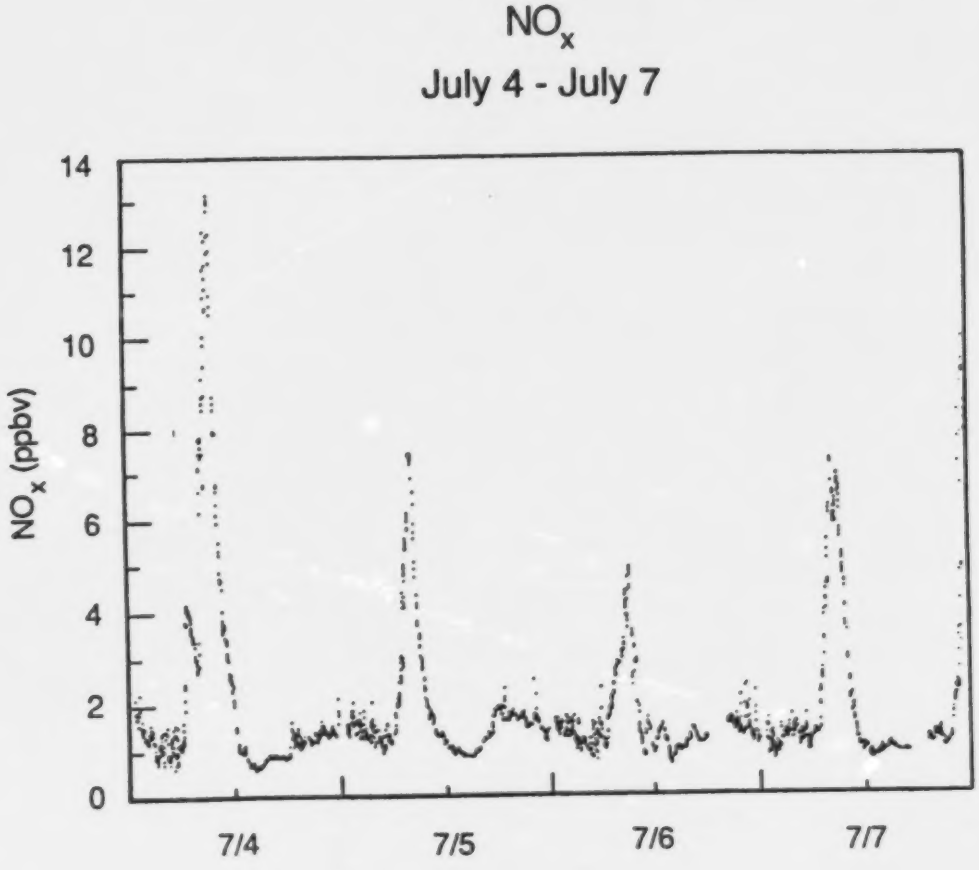


Figure 3 :
The diurnal variation of the $NO_x$ mixing ratio at Scotia, PA for July 4 - July 7 1986.

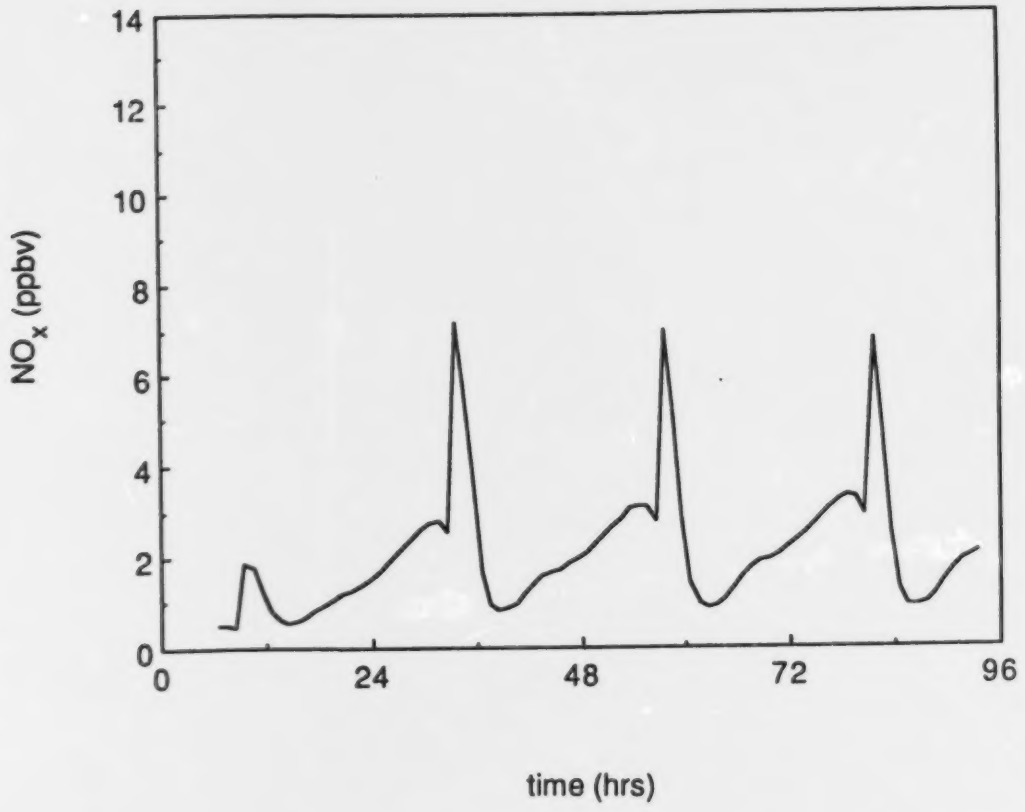


Figure 4 :
The variation of the $NO_x$ mixing ratio during a 4 day period as calculated by the model for the emission scenario described in the text.

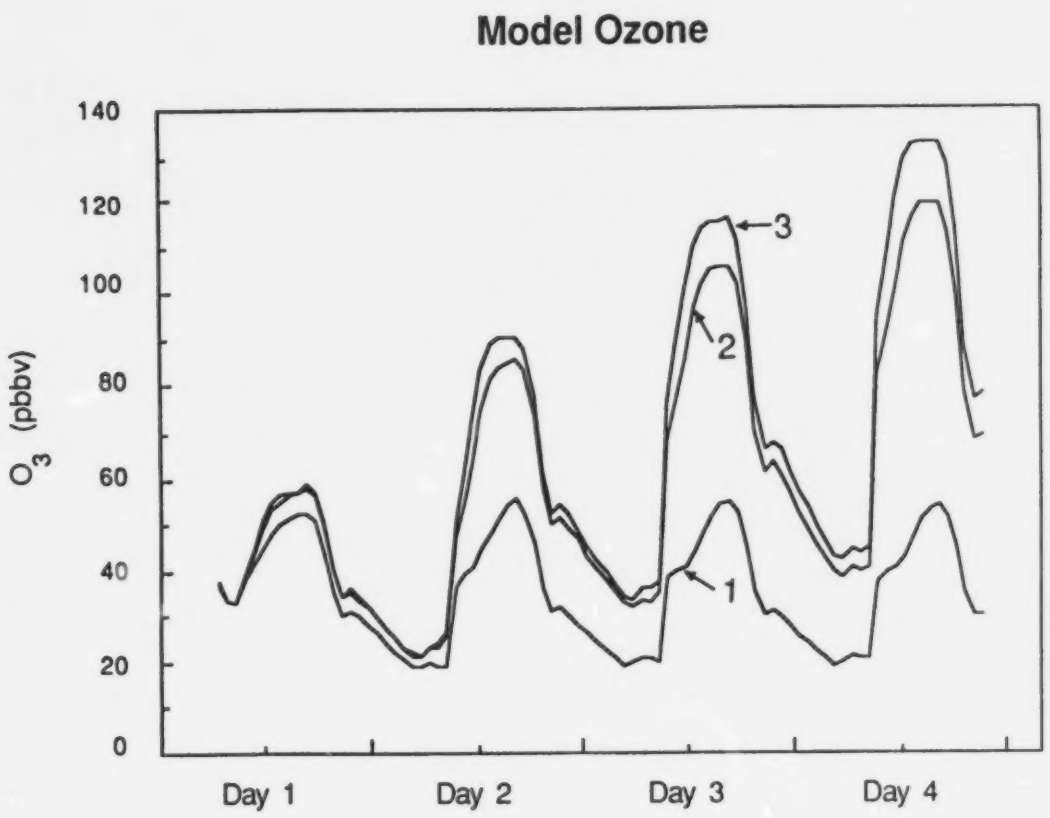


Figure 5 :
Model calculated variation of the $O_3$ mixing ratio during a 4 day period, for the following scenarios : 1) CO, $CH_4$ oxidation only, 2) additional isoprene emission, 3) additional isoprene and anthropogenic NMHC emission.

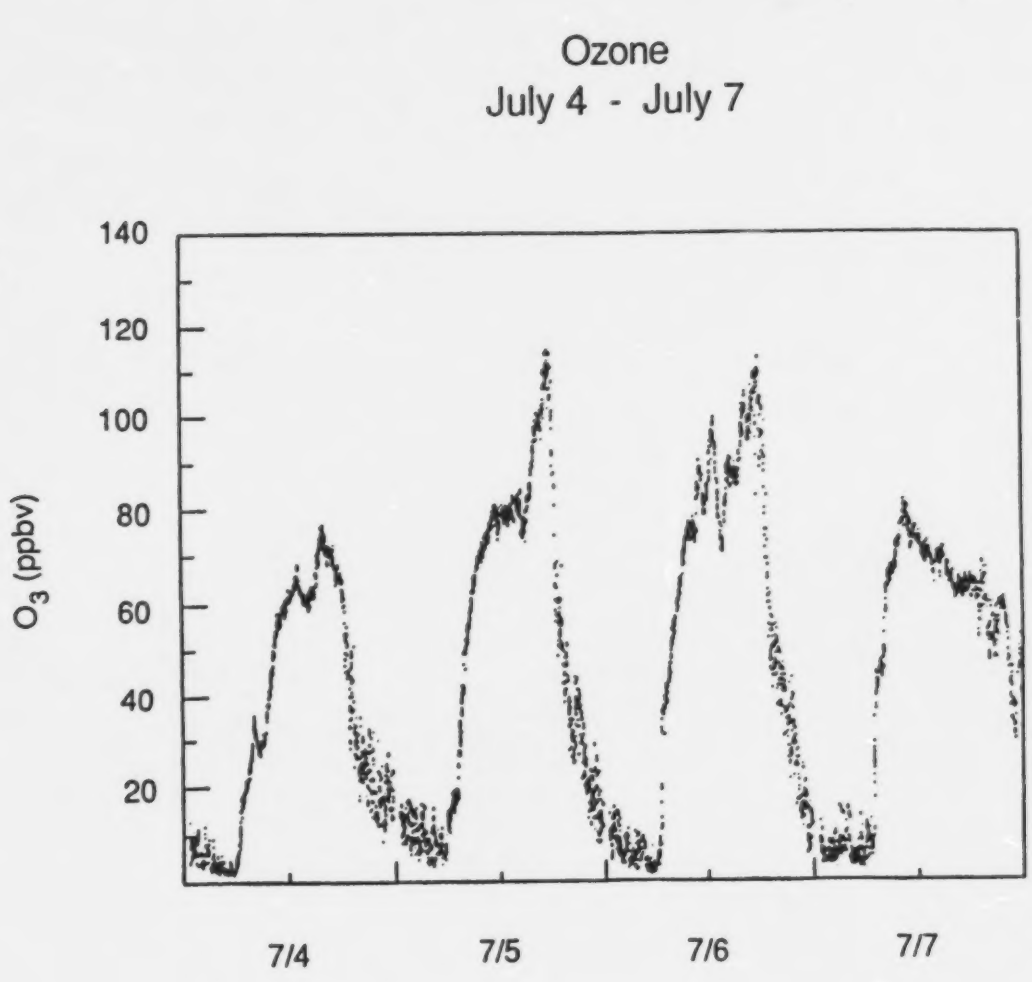


Figure 6:
Observed variation of the ozone mixing ratio at Scotia, PA for July 4 - July 7 1986.

TROISIÈME SÉANCE/SESSION III

TRANSPORT ET MODÉLISATION DES OXYDANTS/OXIDANT TRANSPORT AND MODELING

Président/Chairman

Dr Alan M. Dunker
Environment Science Department
General Motors Research Laboratory
USA

# LE DÉVELOPPEMENT ET LES APPLICATIONS DU MODÈLE RÉGIONAL SUR LES OXYDANTS

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## RÉSUMÉ

L'exposé décrit dans ses grandes lignes le fonctionnement du modèle sur les oxydants régionaux (ROM) de l'Agence américaine pour la protection de l'environnement (EPA) et présente les résultats préliminaires d'une étude sur les répercussions des émissions d'hydrocarbures biogènes sur les concentrations d'ozone dans le nord-est des États-Unis. Les taux maximums d'ozone prévus pour une période de six jours en juillet 1980 correspondent davantage aux concentrations observées lorsque la composante biogène est incluse dans les émissions d'hydrocarbures que lorsqu'elle est omise. Les effets les plus notables des hydrocarbures biogènes s'observent dans les Appalaches, en aval des plus grandes sources de $NO_x$ de la rivière Ohio où les concentrations maximales moyennes d'une heure durant la période de six jours ont chuté de 50 parties par milliard en l'absence d'émissions biogènes.

ABSTRACT

The basic design of the EPA's Regional Oxidant Model (ROM) is described and preliminary results are presented of a study of the impact of biogenic hydrocarbon emissions on ozone concentrations in the Northeastern United States. It is shown that the predicted maximum ozone levels during a six day period in July 1980 agree better with observed concentrations when the biogenic component is included in the hydrocarbon emissions than when it is omitted. The largest effects of the biogenic hydrocarbons occur in the Appalachians, downwind of large $NO_x$ sources in the Ohio River, where peak 1-hour averaged concentrations over the six-day period drop by as much as 50 ppb when the biogenic emissions are shut off.

## INTRODUCTION

The Federal Clean Air Act requires that all regions of the U.S. be in attainment with the National Ambient Air Quality Standards (NAAQS) by the end of this year, 1987. Currently the health-based NAAQS for ozone is exceeded in at least 70 areas, and it is not expected that many of these will have achieved compliance with the standards by the year's end. Figure 1 shows the spatial extent of the ozone problem in the Northeastern U.S. as it existed in 1980. Fig. 1a shows isopleths of the number of days in that year when the maximum 1-hour averaged ozone concentration exceeded the primary standard, 120 ppb. Since the NAAQS for ozone allows only one exceedance of 120 ppb each year, the numbers plotted in Fig. 1a can be interpreted as a rough measure of the severity of the ozone air quality problem. The maximum ozone concentrations observed in 1980 are shown in Fig. 1b. Note that portions of Connecticut and Long Island often experience ozone levels more than twice the primary standard.

The emissions control policies that have been implemented to date have been based on the premise that the ozone problem is a local phenomenon in the sense that the ozone observed in any local area is produced from precursor species (viz, $NO_x$ and hydrocarbons) emitted within that area. This premise is implicit in the current practice of using the EKMA and Airshed models, both of which simulate conditions within individual urban areas, to develop emissions control policies. However, data acquired from field experiments conducted in recent years show that ozone and its precursors can be transported more than 100 km from their point of origin. This finding indicates that the high ozone concentations observed in many areas of the Northeast may be due in significant part to the influx of ozone and its precursors from outside sources. It is possible that the emissions controls now in place have not been as effective in reducing ozone as models had led us to expect

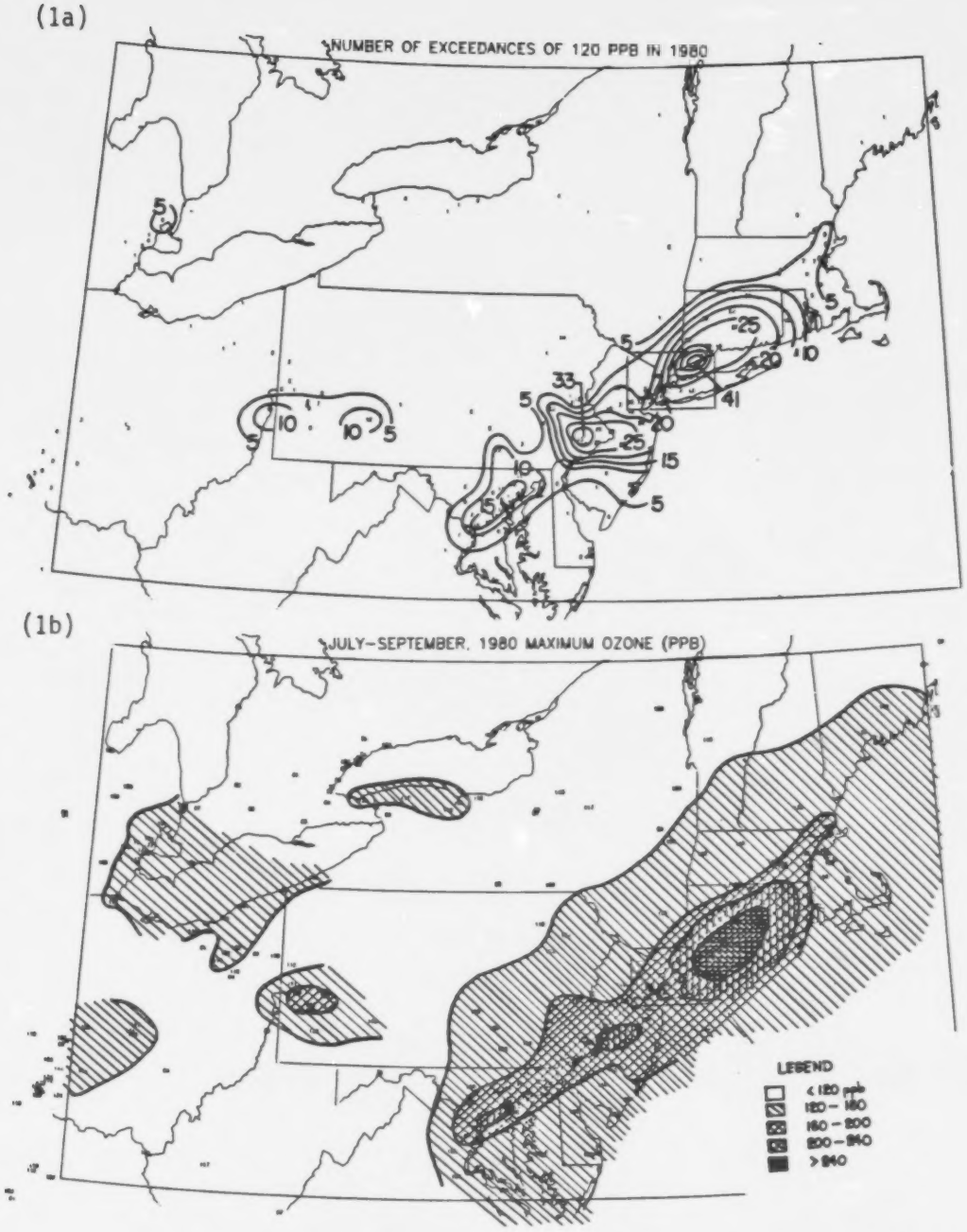



Figure 1. (a) Number of days in 1980 when the measured maximum, 1-hour averaged ozone concentrations exceeded the primary standard of 120 ppb. (b) Maximum 1-hour averaged ozone concentrations observed during July-September 1980.

because the emissions reductions are largely offset by the influx of ozone and its precursors that the modeling studies ignored. In fact, there are certain areas in the Northeast, particularly rural and remote areas of low emissions density, where it is unlikely that the primary ozone standard would be achieved if all local sources were shut down completely.

It was early evidence of the regional character of the ozone problem that led the EPA to begin the development of the Regional Oxidant Model (ROM) in the late '70's. The role envisaged for the ROM was to provide a scientifically credible basis for simulating the regional transport and collective fate of emissions from all sources in the Northeast, and to serve thereby as a tool for developing regional emissions control policies for attaining the primary ozone standard in the most cost effective way. It is now widely believed that the only way to develop effective post-'87 emissions control plans is through the use of a model such as the ROM that treats the regional character of the ozone phenomenon explicitly.

The ROM is now operational but its performance has not yet been fully evaluated. That task, in which model predictions are compared with measured data, is curently underway and its findings will be reported in early 1988. (Some preliminary results will be presented here.) Nevertheless, the ROM has already been called into service in several applications for the EPA's Office of Air Quality Planning and Standards. These applications include an assessment of the effects of proposed VOC and $NO_x$ emissions changes on ozone levels in rural and remote areas, the effects of proposed controls on attainment of various secondary ozone standards presently under consideration for possible promulgation this year, and the impact on ozone of VOC emissions from Treatment Storage and Disposal Facilities of toxic wastes. In addition, we have received requests from other offices of the EPA and other Federal agencies for model applications ranging from estimates of the exposure of the general population to

formaldehyde, to estimates of PAN concentrations in remote forests. Since the number of requests for modeling support that we have already received far exceeds the capacity of our available resources to fulfill, we will attempt in the coming year to develop ways of making the ROM directly accessible to the user community. This will not be an easy task, however. Because being a comprehensive model with detailed descriptions of a multitude of chemical and physical processes over a large geographical area, the ROM is a large complicated model that requires sizable computer and human resources to operate and maintain. For example a single, 24-hour simulation requires about 2 hours of CPU time on an IBM 3090 computer and the input of some 20 million parameter values extracted from a vast array of raw data and submodels.

The purpose of this paper is to provide an overview of the Regional Oxidant Model and to present preliminary findings of a model study currently in progress to assess the effects of biogenic hydrocarbons on ozone levels in the Northeastern United States.

## MODEL DESIGN

### Treatment of Meteorological and Chemical Pro esses

The ROM was designed to treat all of the chemical and physical processes that are known, or presently thought, to affect the concentrations of air pollutants over several day/1000 km scale domains. Among these processes are (not necessarily in order of importance):

1. Horizontal transport;
2. Photochemistry, including the very slow reactions;
3. Nighttime chemistry of the products and precursors of photochemical reactions;
4. Nighttime wind shear, stability stratification, and turbulence "episodes" associated with the nocturnal jet;

5. Cumulus cloud effects--venting pollutants from the mixed layer, perturbing photochemical reaction rates in their shadows, providing sites for liquid phase reactions, influencing changes in the mixed layer depth, perturbing horizontal flow;
6. Mesoscale vertical motion induced by terrain and horizontal divergence of the large scale flow;
7. Mesoscale eddy effects on urban plume trajectories and growth rates;
8. Terrain effects, on horizontal flows, removal, diffusion;
9. Subgrid scale chemistry processes--resulting from emissions from sources smaller than the model's grid can resolve;
10. Natural sources of hydrocarbons, oxides of nitrogen ($NO_x$) and stratospheric ozone ($O_3$);
11. Wet and dry removal processes (e.g., washout and deposition).

When the model development work was initiated some 10 years ago an attempt was made to derive from the observational evidence available at that time an estimate of the minimum vertical and horizontal resolutions necessary to describe the processes listed above. The aim was to arrive at the best compromise between the restrictions imposed upon the model by computer time and memory limitations and the need to describe each process as accurately as possible. We reviewed the nitric oxide (NO), $O_3$ and meteorological data reported in Siple et al. (1977) by the participants of the 1975 Northeast Oxidant Transport Study and concluded that the model would require at least 3 layers (Lamb, 1983a). One layer would treat shear and marine layers during the day and the radiation inversion layer at night. Another layer would simulate the free convective subcloud mixed layer during the day and the reservoir of aged species above the radiation inversion at night. The third layer would represent the convective cloud layer during the day and the zone of cloud residue at night. In addition, it would be advantageous to have a shallow layer adjacent to the ground to simulate dry deposition processes and subgrid

scale chemistry phenomena associated with line and minor point source plumes. However, in order for a model with so few layers to be viable, the layers would have to be "dynamic" rather than static layers of constant thicknesses. That is, the layers would have to be free to expand and contract locally in response to changes in the phenomena they are intended to treat. The Regional Oxidant Model has this property.

Figure 2a shows a cross-section of the model layers along latitude 38°40' on 18 July 1980 at hour 0700 EST just before the radiation inversion (Layer 1) breaks up; and Figure 1b is the same cross-section 3 hours later with cumulus clouds growing in Layer 3. Note that the surfaces that comprise the interfaces of adjacent layers in the model are variable in both space and time, and thus the volumes of each grid cell vary similarly. Note also (Fig. 2a) that mountain tops may penetrate the surface inversion at night and be exposed to species in Layer 2. The concentrations of all chemical species in Layers 1, 2, and 3 are handled prognostically. In Layer 0 they are treated diagnostically. For this reason we often refer to the ROM as a 3 1/2 layer model.

Operating System

All of the chemical and physical processes that occur within the four layers that we discussed above are described by a system of differential equations that constitute the basis of the model's predictions. Computer solvable analogues of these equations comprise what we refer to as the Core model. All of the independent variables that enter these equations, such as wind velocities, layer thicknesses, emission rates, etc, are prepared by a network of some 30 peripheral processors or modules for input to the core model. Some of these modules are rather complex models themselves. For example, one processor generates nighttime wind fields in Layer 1 by solving the shallow water equations, taking into account topography, sea-level pressure, friction effects, and the

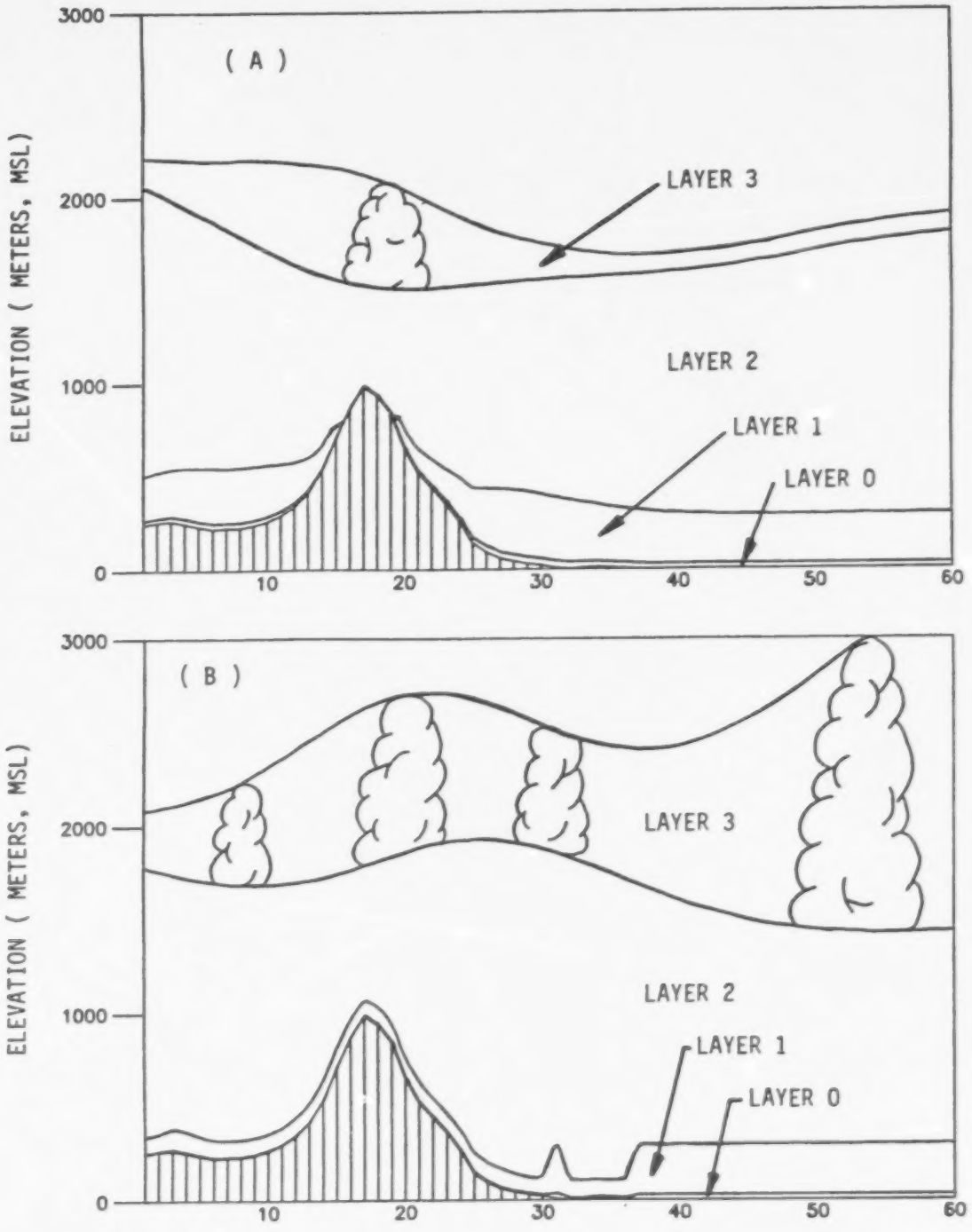



Figure 2. Cross-section through model layers along latitude 38°40' (see Figure 3) at 0700 (a) and 1000 (b) on 18 July 1980. Numbers along abscissa denote grid column.

rate of growth of the radiation inversion layer (Lamb, 1984). Another processor uses observed wind data and physical principles to produce ensembles of wind fields for use in Layers 2 and 3 at night and in all three layers during daylight hours when the surface inversion is absent. By structuring the ROM in this modular fashion, we can change the method used to generate individual variables without having to overhaul the entire model. Even the chemical kinetics mechanism, which is a major component of any photochemical model, is among the interchangeable components. Thus, when we refer to a particular "generation" of the ROM, such as ROM1 or ROM2, we are referring to the network of modules, including the kinetics scheme, that drive the CORE model. The CORE, as described briefly above and in detail in Lamb (1984), will remain fixed for all foreseeable generations of the ROM.

## Quality Assurance Procedures

Another important advantage of a modular model structure is that it facilitates the implementation of quality assurance procedures. The ROM network is so extensive and the quantity of data it generates is so vast that accurate model simulations would be virtually impossible without an adequate means of detecting and correcting errors that inevitably arise in the model operations. We have developed a set of procedures, involving both machine and human checks, that are used to monitor all stages of the model operation from the processors to the core model itself. Considering the great economic cost of the emission control policies that the model is called upon to help formulate, we regard the quality assurance procedures to be one of the most important components of the model program.

Many of the quality control (QC) programs are executed automatically at the completion of each processor execution. The outputs of the QC programs are assigned to reviewers who must certify that all

performance criteria have been satisfied. The generation of the matrix inputs (BMATRIX file) for model execution is not initiated until certified versions of all processor files are available for input to the core model.

A final level of QA checks takes place in the model simulation itself. This consist of an extra, dummy species that is emitted at a fixed rate from a fixed set of source locations, and which decays at a rate proportional to the local photolysis rate of $NO_2$. By design, the concentration of this species everywhere in space and time is a function of the meteorology only. Thus, if two model runs are performed using the same meteorological scenario but different emission rates for the VOC and $NO_x$ sources, as is done in evaluating emissions control strategies, the results of the two runs are deemed to be invalid unless the simulated concentration of the dummy species is identical in both runs at every grid point and time step. Because the lack of equivalence signals the presence of an error in the model input data, which must be found and corrected before the actual effects of the source emissions changes can be assessed accurately.

## Key Processors

Following are brief descriptions of some of the principal components of the input processor system that constitutes the present version of the ROM, i.e., ROM2.

### Chemical Mechanism

ROM2 uses a compressed version of the explicit Carbon Bond X chemical kinetics mechanism. The compressed version, which is known as Carbon Bond IV, was developed specifically for the ROM (Whitten, et al, 1985). It contains 70 reactions among 28 chemical species, including the following eight reactive hydrocarbon groups: FORM (formaldehyde), ALD2 (higher

aldehydes), ETH (ethene), OLE (propene and other olefins), TOL (toluene), XYL (xylene and other aromatics), PAR (paraffins) and ISOP (isoprene). The last species allows explicit simulation of the organic compounds emitted by vegetation. We will discuss this feature of the ROM in more detail later in this paper.

Eight of the chemical species simulated by the Carbon Bond IV mechanism undergo photolytic reactions. The estimates of the rate constants for these reactions used in ROM2 are based on theoretical values of the actinic solar flux in the lower troposphere (Demerjian, et al, 1980) which are modified using the scheme of Jones, et al, (1981) to account for the effects of clouds. Each of the rate constants is an explicit function of elevation in the model.

Sources

Just as the nature of meteorological processes determines the vertical resolution requirements of the model, the joint characteristics of the sources and chemistry are a major factor in determining the horizontal resolution of the grid and the emissions inventory. In order to model ozone accurately, it is necessary for the model's grid size to be small enough to resolve the "granularity" of the VOC and $NO_x$ source distributions. If the grid size is so large that major sources that are actually separated from each other in space are mixed together within a single grid cell, essential nonlinear characteristics of the chemical processes that act upon the emission will be lost and systematic errors in predicted ozone levels will result. Studies reported by Lamb (1986b) showed that the magnitude of simulated peak ozone concentrations decreased sharply with increasing grid size, and that the sensitivity of the model to changes in VOC and $NO_x$ emissions was attentuated by increasing the grid size. The grid size chosen for the ROM is $\Delta \approx 18$ km (1/4° longitude x 1/6° latitude). This choice represents a compromise between the desired

resolution and the corresponding computer time required to simulate the desired spatial domain, shown in Figure 3. Analyses of the NAPAP 4.2 emissions inventory reported in Lamb (1986a) indicate that with $\Delta \approx 18$ km, the ROM can resolve at most 83% of the peak urban-scale VOC source strength and 78% of the corresponding $NO_x$ strength in the Northeast (Figure 3). For comparison, the corresponding numbers for a grid size $\Delta = 80$ km are 33% for both VOC and $NO_x$; and for grids larger than about 200 km, the resolution is not significantly better than that of a single box covering the entire domain.

In the current model, ROM2, gridded anthropogenic emissions estimates are based on the NAPAP 5.2 inventory with VOC's speciated into the eight Carbon Bond IV classes defined earlier. The anthropogenic emissions data are supplemented with gridded biogenic hydrocarbons emissions estimates prepared in our laboratory by Novak and Reagan (1986). These estimates were developed using (1) emissions factors for isoprene and monoterpenes reported in the literature for each vegetation species; (2) empirical relationships between the emissions factors and environmental parameters such as temperature, sunlight intensity, soil conditions, geographic location, etc; and (3) quantitative estimates of the biomass (dry foliar weight in grams) of each species in each grid cell. The biomass estimates of 61 species of trees, 10 types of crops and 2 groups of grasses were derived from detailed analyses of data from the Forest Service, Agriculture Department, and other sources. The resulting, hourly biogenic hydrocarbon emissions estimates are split into the Carbon Bond IV groups as follows:

1 mole monoterpene = 1 mole OLE + 8 moles PAR

1 mole isoprene = 1 mole ISOP + 1 mole PAR

We will return to these data later in the paper.

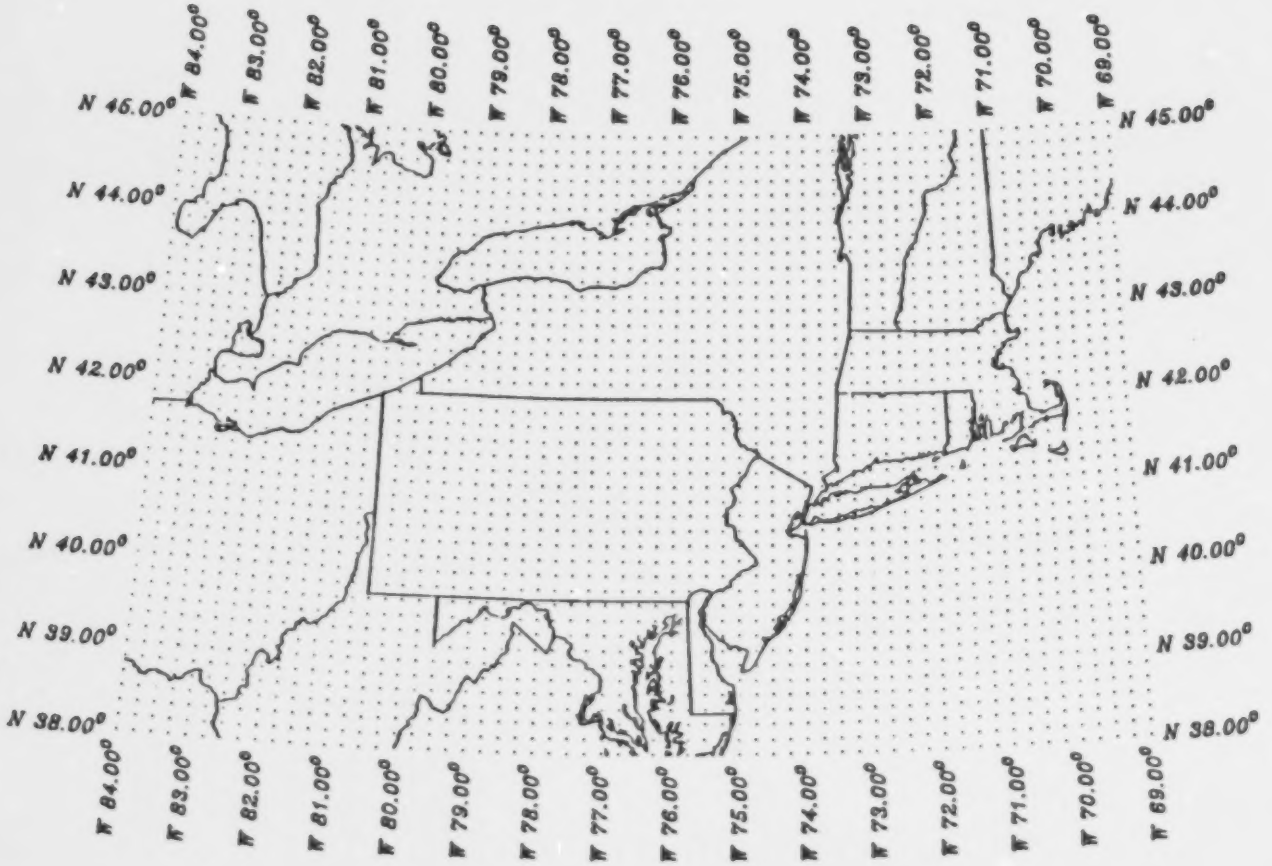



Figure 3. Modeling domain simulated by ROM2. Each dot represents a grid cell.

Meteorology: winds

Layer averaged horizontal winds are prepared for input to the Core model by two separate submodules designated P11 and P7 in the processor network. The former, based on the scheme described in Lamb and Hati (1987), generates winds for layers 2 and 3 at all hours and for layer 1 at all times when at least 50% of the surface wind stations are reporting wind speeds greater than 2 m $sec^{-1}$. The wind fields generated by this processor have four specific properties: (1) they agree exactly with measured winds at all sites at which observed wind speeds and directions are specified; (2) the horizontal divergence of the flow satisfies prescribed input values; (3) the kinetic energy associated with spatial fluctuations of given scale satisfies specified profiles in wave number space; and (4) the total kinetic energy of the flow conforms as closely as possible to a given value without violating the first three conditions. This processor has the capability of generating ensembles of wind fields for use in running the ROM in a "probabilistic" mode in which the probability distribution of concentration values is predicted. Figure 4 shows an example of the wind fields P11 produces. During times when more than 50% of the surface wind stations are reporting speeds less than 2 m $sec^{-1}$ (usually nighttime and early morning hours), layer 1 winds are derived from submodule P7 which simulates the motion and depth of surface radiation inversions using the shallow water equations. Figure 5 shows an example of the flow field produced by P7. This approach is based on the view that during inversion conditions, surface wind data are not representative of the bulk motion of the inversion layer, especially when the measured wind speeds are very low. It is assumed that in these cases the surface pressure field, terrain elevations, cooling rate and surface roughness combined with physical laws provide a more accurate description of the transport of material in the surface layer than one can deduce from the wind observations.

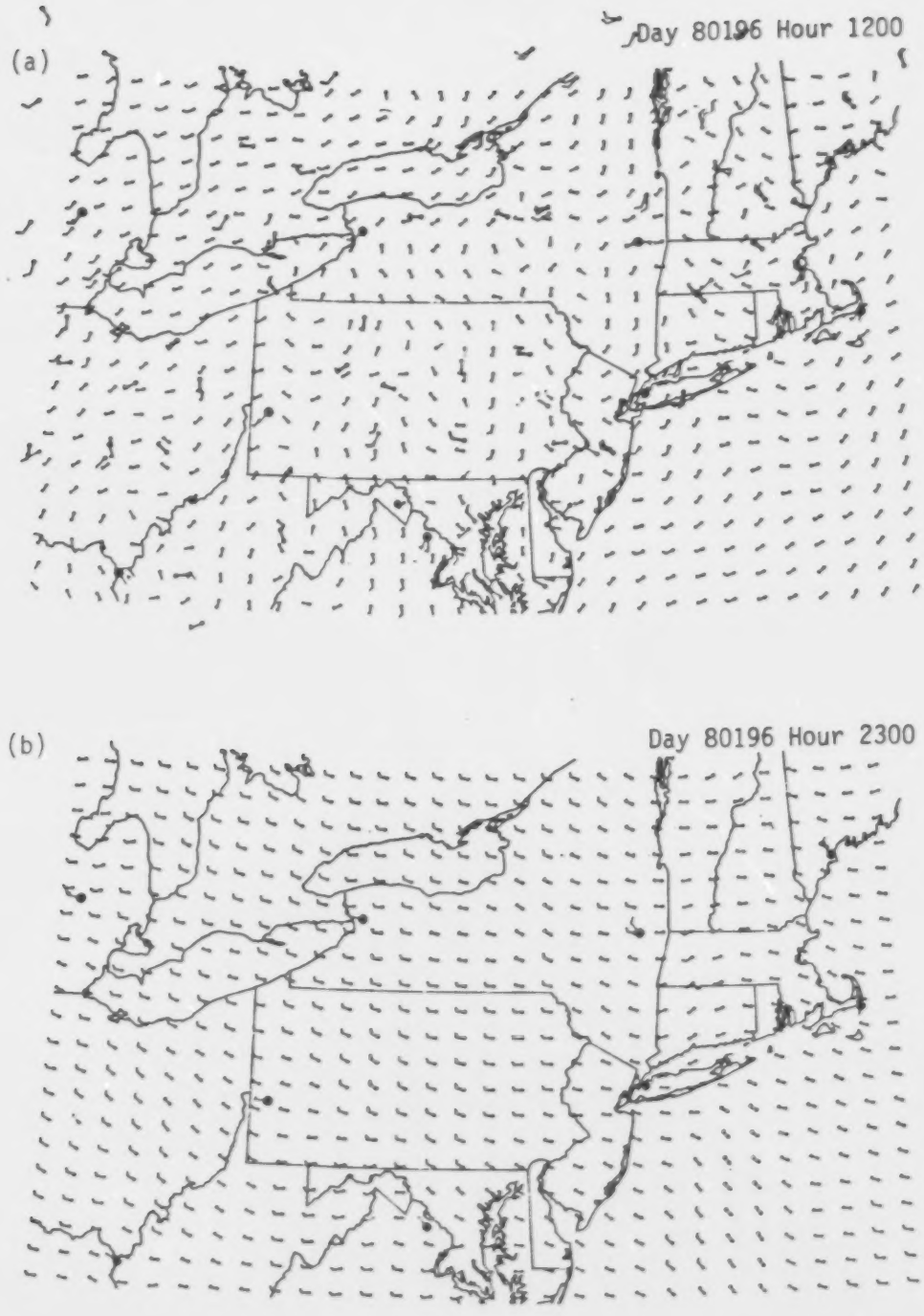



Figure 4. (a) Wind field in Layer 1 generated by processor P11. Values are plotted at every other grid point. Irregularly spaced wind symbols indicate surface wind observations used by P11 to produce the complete flow pattern.
(b) Same as (a) except flow is in Layer 3.

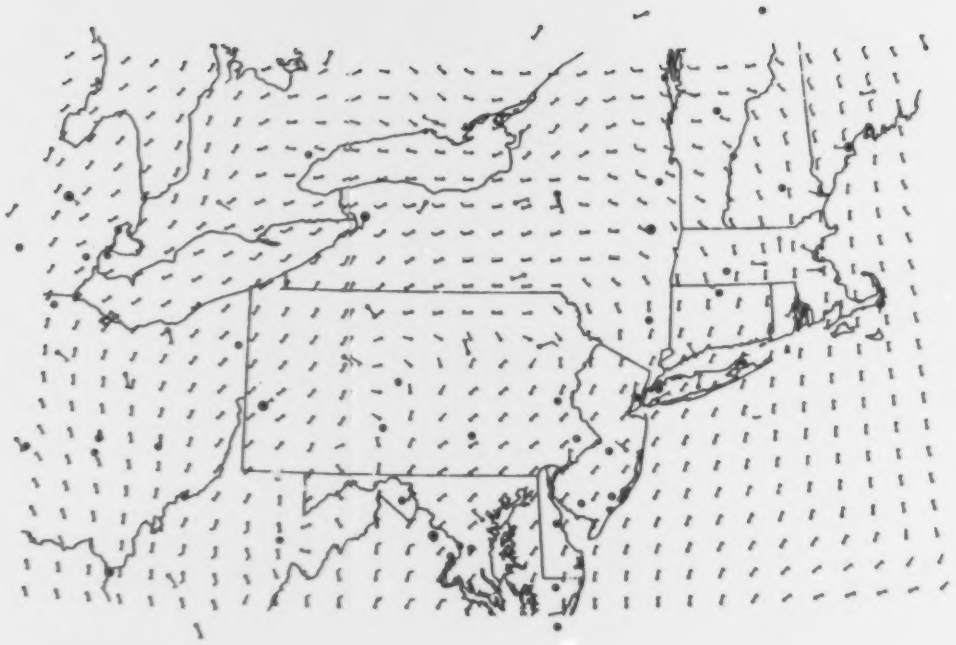


Figure 5. Example of the inversion layer (Layer 1) wind field generated by processor P7 for day 80196 hour 0600. Surface wind observations shown in the figure were not used to produce the flow field.

Meteorology: layer interface elevations

When a surface inversion is present (indicated by a majority of surface wind stations reporting speeds less than ? m/sec), the top $z_1$ of Layer 1 is defined to be the top of the inversion layer. In this case $z_1$ is computed by processor P7 referred to earlier. The predicted value is a function of the simulated flow in the inversion layer and the surface cooling rate, which is given a constant uniform value based on measurements reported by Godowitch and Ching (1980) of inversions in the St. Louis area. When a surface inversion is not present, $z_1 = z_T + \min(300\ m, |L|)$, where $z_T$ is the local terrain elevation and L is the local Obukov length. In this case Layer 1 represents the shear layer in which the wind speed and direction is significantly different from that at higher levels. The top $z_2$ of Layer 2 is defined as the top of the convective mixed layer when cumulus clouds are absent and the elevation of cloud bases when cumulus are present. In cloud-free conditions, $z_2$ is the elevation $z_H$ at which the potential temperature exceeds the surface temperature by 1°C. This is the Holzworth method (see Holzworth and Fisher, 1979) which was found by Shipham (1983) to give more accurate estimates of measured dry mixed layer tops than a number of other techniques. When cumulus clouds are present, the lifting condensation level $z_{LCL}$ is computed at each grid site using the pseudo temperature, dew point and pressure soundings. If $z_{LCL} < z_H$, then $z_2 = z_{LCL}$; otherwise $z_2 = z_H$. The top $z_3$ of Layer 3 is defined to be the local elevation of the tops of cumulus clouds computed using a scheme developed by Vukovich and Haws (1986). If clouds are absent, $z_3 = z_2 + 100m$.

Interface material fluxes

There are four separate processes that can cause species to move from one model layer into an adjacent layer: (1) nonzero mean vertical air motion; (2) turbulence, including cumulus cloud updrafts; (3) changes in the elevation of surface interfaces; and (4) horizontal wind at

locations where the interfaces have nonzero horizontal slope. The mean vertical air speed is computed in the ROM processor network using the air mass continuity equation, terrain elevations and the horizontal wind divergences discussed earlier. Vertical turbulence velocities are estimated using empirical and theoretical expressions mentioned below. Cumulus cloud updraft speeds are provided by the Vukovich-Haws scheme referred to earlier. Tne time rates of change and horizontal slopes of all layer interfaces are derived by straightforward differencing methods.

Horizontal diffusivity, vertical turbulence, and deposition velocities

Estimates of all parameters associated with turbulence phenomena are based on empirical and theoretical formulas that require land use and cloud cover data in addition to meteorological information already discussed. The land use data base used by the ROM specifies the fraction of the surface area of each grid cell that is engaged in each of 8 land use categories: urbanized area, agricultural land, rangeland, deciduous forests, coniferous forests, mixed forest (including forested wetland), nonforested wetlands, mixed agricultural and rangeland, and water. Each of these categories is assigned a surface roughness, based on the work of Sheih et al (1979); an albedo, based in part on Geiger (1966) and Munn (1966); and a deposition resistance for each chemical species simulated by the ROM. The last parameter values are taken from empirical data summarized by Hill and Chamberlain (1976). These data cover only a limited group of chemical compounds and only a few surface types. Therefore, many of the deposition resistance values used in the ROM are estimates based on chemical reactivity information and similarity with other species for which measured values are available.

The land use, surface roughness $z_0$ and albedo $\alpha$ data are aggregated to produce net values of $z_0$ and  for each grid cell. These are combined with local solar zenith angle, cloud cover and surface wind speed values for input into the scheme of Holtslag and Van Ulden (1983)

to estimate the surface sensible heat flux H and Obukhov length L at each hour at each grid cell that is predominantly over land. Over water, H and L are estimated using the air temperature, extrapolated by the Barnes (1973) method from land based measurements, and the local surface water temperature input for each of the Great Lakes and Atlantic Ocean from NOAA satellite measurements. Once the Obukhov length is estimated it is combined with the local surface roughness and wind speed values to derive the friction velocity $u_*$ using the method of Melgarejo and Deardorff (1974). These values combined with local relative humidity and deposition resistance estimates provide the deposition velocities for each species at each hour following the technique of Sheih, et al (1979). During daytime hours over land, the local values of L, $z_o$, wind speed and mixed layer depth yield vertical turbulence velocity profiles using convective scaling similarity theory (see Nieuwstadt and van Dop (1982)). In the ROM the horizontal diffusivity is proportional to $w_* h_2$ during convective conditions, where $w_*$ is the convective velocity scale, and it is zero at all other times.

Other meteorological parameters

There are numerous additional features of the ROM that cannot be described in the limited space of this paper. They include the parameterization of subgrid scale chemical processes associated with line and minor point sources, the transport of emissions directly from Layer 0 into Layer 3 by cumulus cloud updraft roots, plume rise of major point sources, deposition on mountains, and others. Further details on these features of the model can be found in Lamb (1983a, '84).

Initial and boundary conditions

This is another topic that can we can describe in only a superficial way here (see Lamb, 1986 for further information). Basically,

all simulations performed with the ROM use meteorological data from historical periods that begin on a day when the median of the 1-hour averaged ozone concentration measured at all sites in the model domain was near its seasonal minimum value. This permits us to initialize all species (except ozone) with "clean" troposphere values without incurring an unnecessarily large error penalty. Data are simply not available for all the species simulated by the ROM over the vast 3-D domain that it treats to initialize concentrations in a rigorous way. The initial value used for ozone is uniform over the domain and its magnitude is selected as the mean value of the daytime measured values. The same "clean" troposphere values are also used at the model inflow boundaries during the simulation period, with the exception of ozone which is handled as follows. Monitoring sites have been identified near the southern and western boundaries of the model whose measurements are considered to be "representative" of the mesoscale air mass. Records from the stations are divided into daytime (0700-2000) and nighttime (2000-0700) portions. The averaged daytime value is used as the inflow boundary condition (BC) for model Layers 2 and 3 for 24 consecutive hours (beginning at 2000 the previous day) and it is used as the BC in Layer 1 during the hours 0700-2000. The average measured nighttime ozone level is used as the BC in Layer 1 only and only for the hours 2000-0700.

## ROM APPLICATIONS

Meaningful applications of a model such as the ROM involves much more than simply supplying values for the input parameters and executing the code. There are numerous issues with which one must deal, but in general these constitute two basic questions: What quantitative information is a regional scale model like the ROM capable of giving? How reliable is the information it gives? The first of these questions involves among other points the inherent stochastic nature of atmospheric modeling and the ability to infer long-term averages and liklihood estimates from a finite set of short-period model simulations. The reliability question involves the level of uncertainty in model input data, particularly the emissions data; and our basic inability to measure the accuracy of a model's ability to predict differential as opposed to absolute concentrations. We have already found that one of the most serious present obstacles to the use of models in emissions control strategy development is the large level of uncertainty in emissions data. (An example will be shown later in this paper.) Until we have accurate knowledge of the locations and strengths of the existing sources of ozone precursor species, we will not be able to place confidence in control strategies formulated with the aid of a model, regardless of how scientifically competent the model might be. Further discussion of the issues cited above can be found in Lamb (1986) and further discussion will be forthcoming.

Our goal in the remainder of this paper is to present preliminary results from a brief application of ROM2 that centers on the role of biogenic hydrocarbons in ozone formation in the Northeastern U.S. This study represents the first time that a detailed, spatially and temporally variable inventory of biogenic hydrocarbon emissions has been incorporated into a regional scale model. Our aims, therefore, are twofold: to determine whether overall, the estimated biogenic emissions

levels are reasonable; and assuming an affirmative answer to the first question, assess the contribution of biogenic hydrocarbons to peak ozone levels over the Northeast. Within the limited scope of this study we answer the first question by testing whether the addition of the biogenic hydrocarbon emissions to the anthropogenic sources improves or degrades the accuracy of the model's ozone predictions, and whether the predicted concentrations of isoprene, which is predominantly from biogenic sources, is within the range of values that is commonly measured.

Figure 6 compares the total anthropogenic and biogenic hydrocarbon emissions rates integrated over the entire model domain (shown in Fig. 3). Total $NO_x$ emissions are also shown. The anthropogenic data are from the NAPAP 4.2 inventory while the biogenic data are those reported by Novak and Reagan (1986) assuming full sun conditions over the entire model domain. The data show a pronounced diurnal variation in the strengths of the anthropogenic and biogenic sources with both attaining maximum stengths around midday. The data also show that both sources contribute roughly equal amounts of hydrocarbons to the atmosphere. This result is quite surprising considering the heavy industrialization and large population of the region in question. Altshuller (1983) and others have challenged the accuracy of the emissions factors for biogenic hydrocarbons estimated in experimental studies, some of which were used in the preparation of the data shown in Fig. 6, on the grounds that they imply concentration levels for isoprene and monoterpenes much larger than the values that are actually measured in the atmosphere. We will return to this point later.

Fig. 7a shows the top fifty hydrocarbon (VOC) and the top fifty $NO_x$ emitting counties in the Northeast based on 1980 emissions density data (anthropogenic only) documented by Toothman, et al (1984). The union of these two sets is composed of 70 counties, and together they produce about one-half of all anthropogenic VOC and $NO_x$ emissions in the

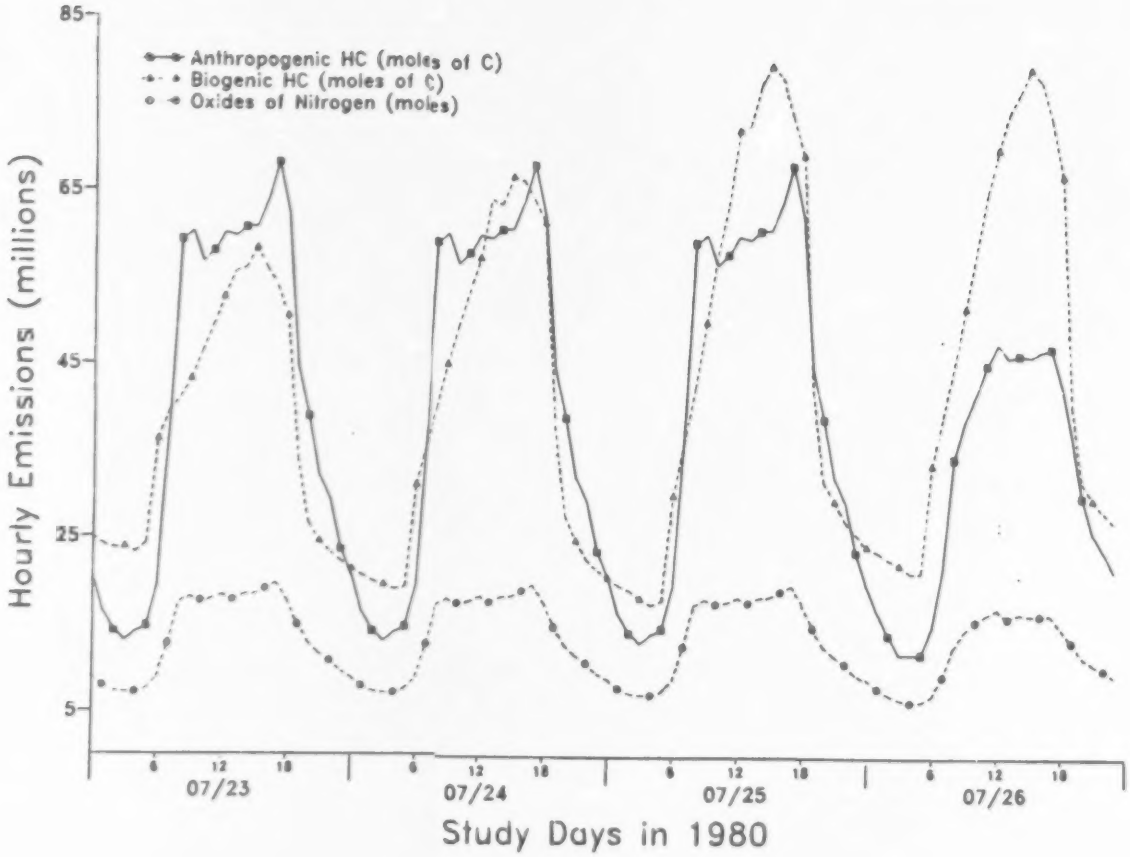
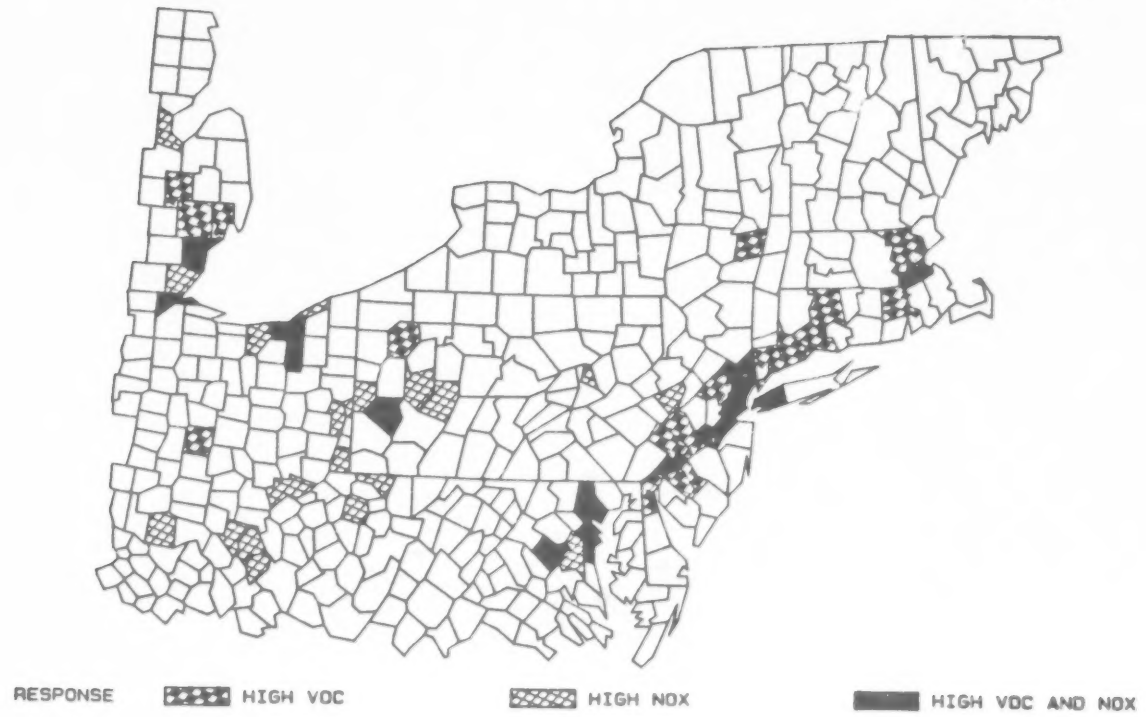



Figure 6. Estimated anthropogenic and biogenic hydrocarbon emissions integrated over the model domain (Figure 3) as a function of time. Integrated $NO_x$ emissions (anthropogenic only) are also shown.



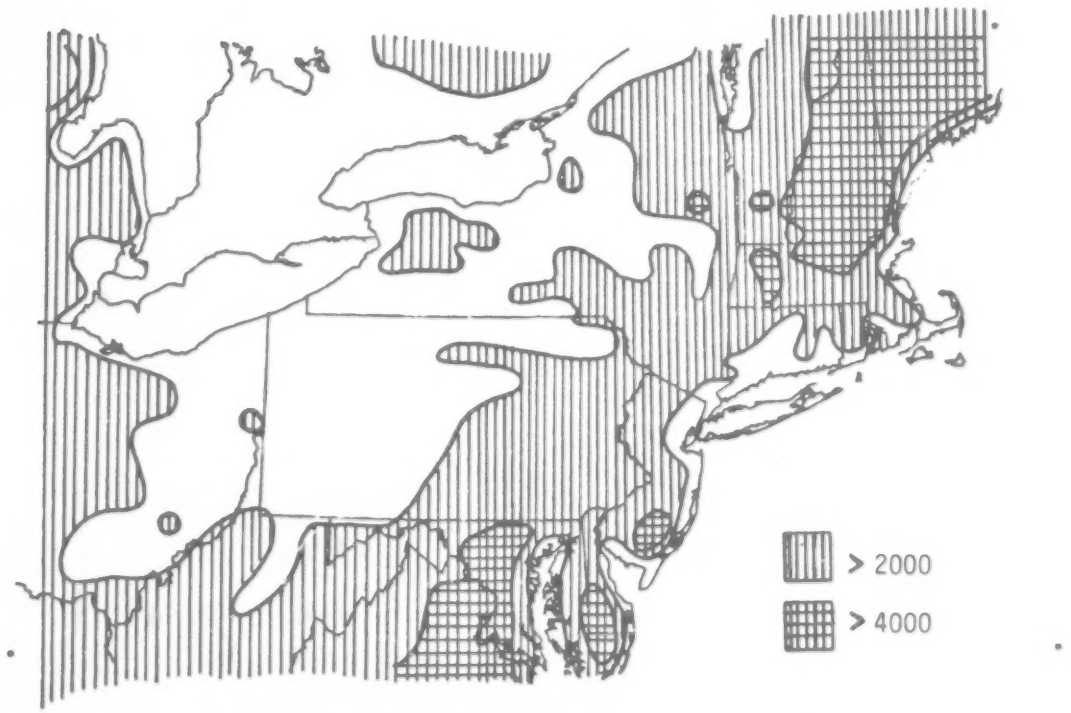




Figure 7. (a) Fifty top county sources of VOC and NOX based on emissions density Q (moles/area/time). Thirty counties are members of both groups. (anthropogenic sources only); (b) Emission rate (moles/hour/grid cell) of the lumped olefin species OLE from biogenic sources at 1400 EST on Day 196, 1980.

model area (Fig. 3), excluding Canada. Note that most of the major $NO_x$ sources are along the Ohio River Valley.

Figure 7b gives a general view of the spatial distribution and strength of biogenic hydrocarbon sources. This figure shows the emission rate of the lumped species OLE, which is used in the model along with PAR as a surrogate of monoterpenes. The emission rates shown in the figure are for a midday hour when the biogenic sources are most active. Note that typical rates are of the order of 2000 moles/hr (per grid cell ≅ 18.5 x 18.5 km). By contrast, OLE emissions from anthropogenic sources in the major urban areas are 3 to 10 times larger.

As a first step in evaluating the accuracy of the biogenic hydrocarbon estimates, let us compare the model's predicted peak ozone concentrations with observed values with and without the biogenics present.

Fig. 8a shows the maximum 1-hour averaged ozone concentrations measured at some 200 SAROAD stations during the period 12-17 July 1980. Since measured concentrations are not available over the entire model domain, to facilitate a comparison of the observed and predicted values we show in Fig. 8b the isopleth pattern that we would have gotten in Fig. 8a had we used the model predicted peak concentrations (with biogenics) at the SAROAD sites in place of the measurements. The agreement in both the spatial patterns and magnitudes is good everywhere except in New Jersey and an adjacent portion of Pennsylvania where the predicted peak concentrations are lower than the levels observed. This discrepancy may be due largely to errors in the VOC emissions of several sources in the Philadelphia area that were discovered after this model simulation was performed. We estimate that the level of uncertainty in existing emissions data is at least as large as the magnitude of the emissions changes that are contemplated in proposed control strategies. This is obviously an unacceptable situation and increased attention is now being directed to

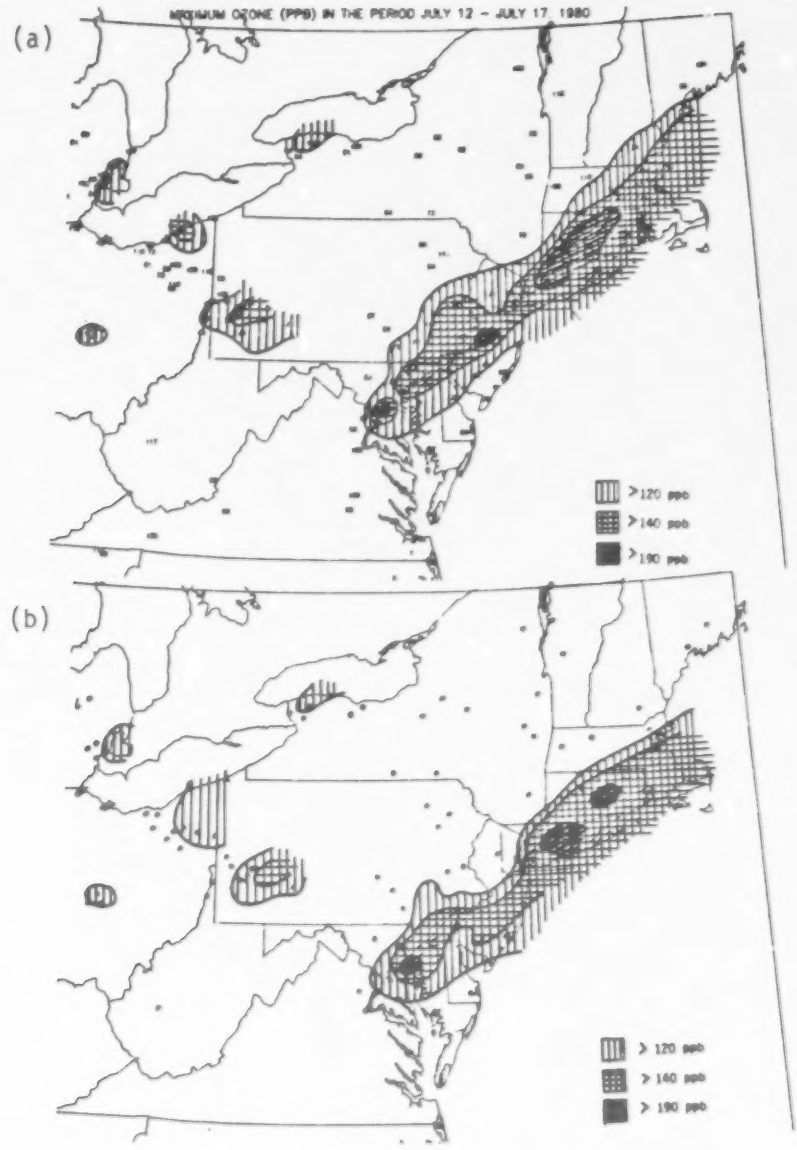



Figure 8 (a). Maximum measured 1-hour averaged ozone concentration at SAROAD sites during the period 12-17 July 1980;
(b). Same as a except model predictions replace measured values at SAROAD sites.

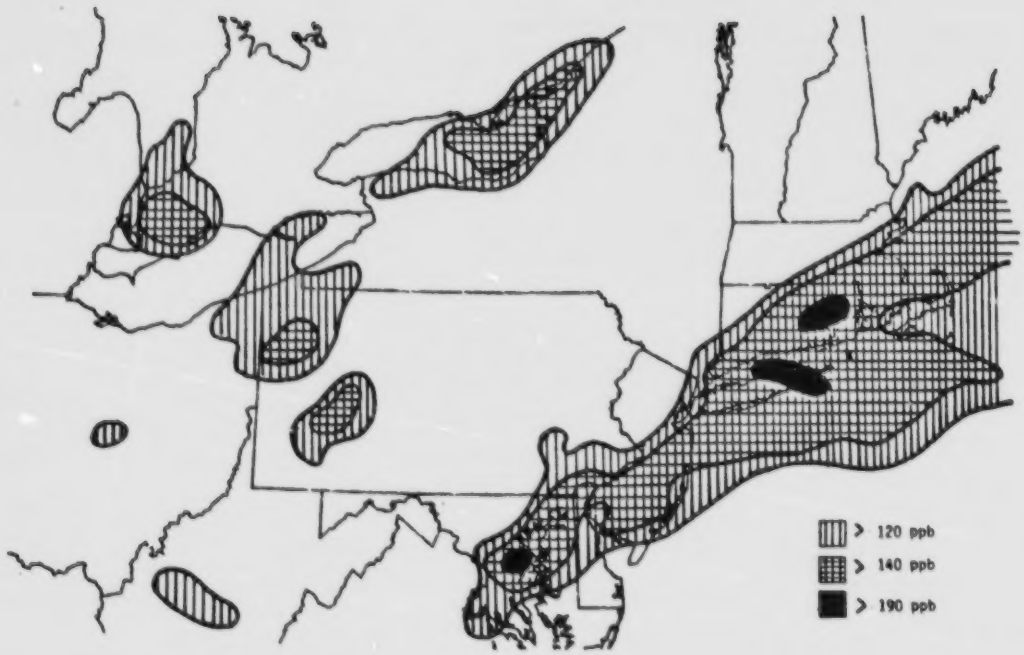



Figure 8 (c). Maximum predicted 1-hour averaged ozone concentration during the period 12-17 July 1980. This figure shows the complete picture of the ozone concentration whereas Figure 8(b) portrays it from the perspective of the SAROAD station sites only.

improving the methodologies used to estimate emissions rates. We plan to investigate the sensitivity of the model predictions to uncertainty in the emissions in the hope of developing guidelines for specifying the maximum allowable error level.

The agreement between the observed and predicted (with biogenic) six-day peak ozone concentrations seen in Fig. 8 is apparent also in Figure 9, which compares the observed and predicted peak ozone each hour during the six-day period 12-17 July 1980. The observations are over all 200-plus SAROAD sites while the predicted values cover all 2520 surface grid cells. The magnitudes of the predicted and observed daily peak values are in good agreement over the entire period except day 198 when an observed value of 285 ppb was observed but only 210 ppb was predicted. This observation is in the upper 0.5 percentile of the values measured all season and it is associated with a plume much narrower than the ROM's 18 km grid can resolve. We noted earlier that attentuation of extreme concentrations is expected because the ROM grid is not small enough to resolve fine scale granularity in the source distribution. An encouraging aspect of the predicted peak values shown in Fig. 9 is the agreement between the phases of many of the peak and secondary peaks in the observations and corresponding features in the predicted values. We add that the predicted peak values remain much higher than the observations at night because many of the model's grid cells are over large water bodies where the ozone is free of the scavenging effects of $NO_x$ emissions. (The subset of model results for only the grid cells containing the SAROAD stations was not available at the time of this writing.)

When the biogenic hydrocarbon emissions are shut off and the same six-day model run is repeated, the predicted peak ozone concentrations drop to the levels indicated by the dash-dot curve in Fig. 9. The spatial pattern of the change in the six-day peak value is shown in Fig. 10. The isopleths are of the difference between the predicted six-day

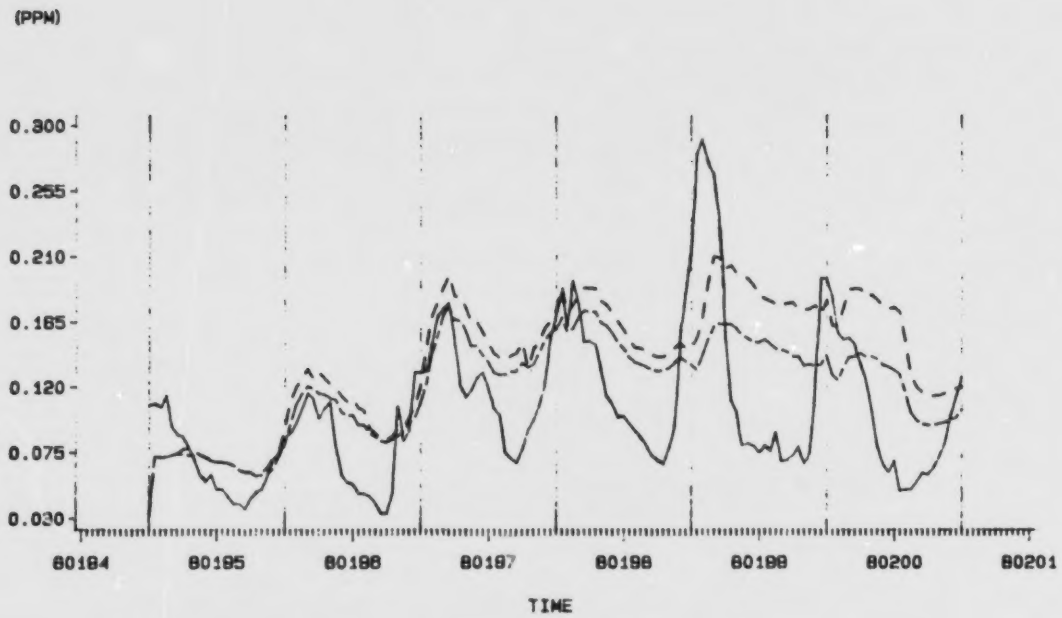



Figure 9. Observed and predicted maximum ozone concentrations each hour during the simulation period 12-17 July 1980. The observed data (solid line) are over 200 plus SAROAD sites while the predicted values are over all 2520 surface grid cells. The dashed curve represents the model results with biogenic hydrocarbon emissions included. The dash-dot represents the corresponding values with biogenics omitted.

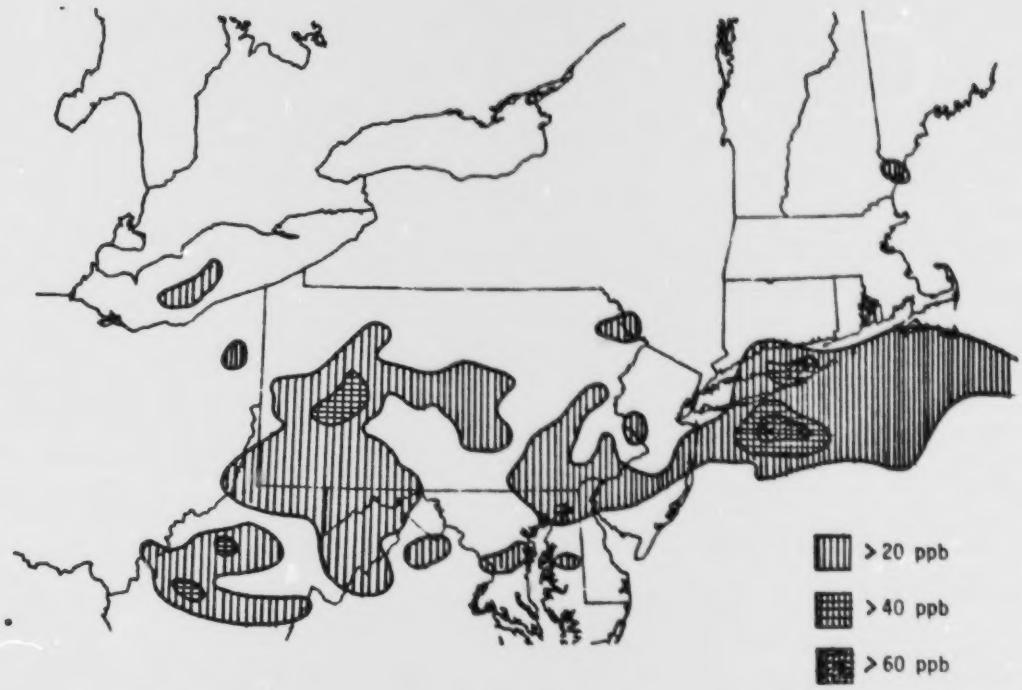



Figure 10. Difference between the six-day peak ozone concentration predicted with biogenic hydrocarbon emissions active, i.e., the concentrations shown in Fig. 8c, and the corresponding values predicted with the biogenic emissions shut off.

peak values shown in Fig. 8c that were obtained with the biogenics "on" and the corresponding values produced by the model with the biogenic emissions shut off. Except for the area of large reduction over the Atlantic Ocean downwind of the erroneous Philadelphia sources mentioned earlier, the largest effect of the biogenic hydrocarbons on ozone are seen in the Appalachians, downwind of the major anthropogenic $NO_x$ sources shown in Fig. 7a. Northeast of Pittsburgh the peak ozone concentration drops 50 ppb when the biogenic emissions are eliminated. We found earlier (Fig. 8a, b) that with the biogenic emissions included, the model predictions in this geographical area were in agreement with observations. This fact and comparisons of the observed and predicted ozone levels at other locations lend support to the accuracy of the biogenic hydrocarbon emissions estimates and to the treatment of their chemistry in Carbon Bond IV.

Further supporting evidence is given by the peak isoprene concentration predictions shown in Fig. 11. Being highly reactive with both OH and $O_3$, isoprene concentrations peak near midday when the emissions are strongest (see Fig. 6) and decay to very low levels at night. Although no measurements are available for direct comparison, the peak levels predicted are well within the range of measured values summarized by Altshuller (1983). They are also consistent with the recent measurements reported by M. Trainer earlier in this conference.

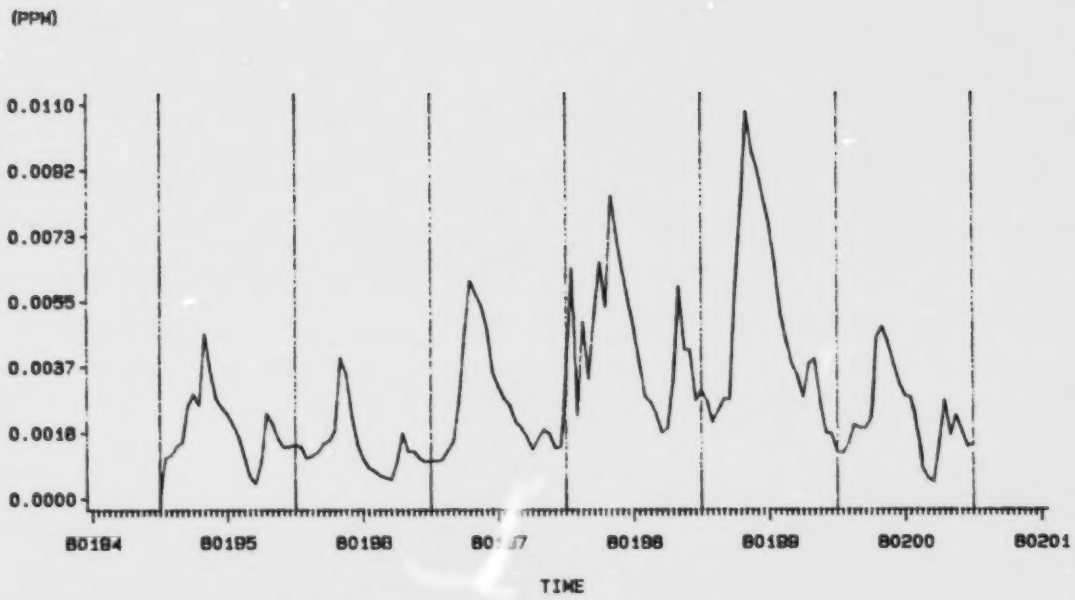



Figure 11. Predicted peak isoprene (ISOP) concentration over the entire model domain in Layer 1 at each hour of the six-day simulated period. Measured concentrations summarized by Altshuller (1983) are in the range 0.001 to 0.010 ppm.

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# THE PRODUCTION AND TRANSPORT OF OXIDANTS DURING LONG RANGE TRANSPORT

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## RÉSUMÉ

Le modèle eulérien STEM-II, qui comporte des modules de transport, de chimie et de dépôts permet d'étudier le transport des oxydants à échelle moyenne et régionale. Ce modèle tient compte de 55 espèces chimiques contenues dans les gaz, les nuages, la pluie et la neige; son application principale concerne l'étude du transport des oxydants et de leur formation dans des conditions météorologiques à échelle synoptique. Une analyse effectuée à partir de ce modèle est actuellement en cours pour vérifier l'exactitude d'une étude sur le terrain au Japon visant à caractériser l'incidence des émissions provenant de la région métropolitaine de Tokyo sur la qualité de l'air d'un important lieu de vacances et forestier d'une région montagneuse près de 200 kilomètres plus loin. Les résultats de cette étude font l'objet d'une discussion.

# The Production and Transport of Oxidants During Long Range Transport

by

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## ABSTRACT

The STEM-II Eulerian, combined transport, chemistry and removal model is being used to investigate the transport of oxidants on meso- and regional-scales. The model treats 55 chemical species in the gas, cloud, rain and snow phases. Oxidant transport and formation under synoptic scale meteorological conditions is one of the current applications of the model. Diagnostic model analysis is being performed in support of an intensive field study in Japan characterizing the inpact of emissions from a large metropolitan area, Tokyo, on the air quality of an important resort and forest area located in a mountainous region ~ 200 km away. The results of this study are discussed.

## I. Introduction

The STEM-II model is being used to investigate oxidant formation and transport on meso and regional scales. One application is the investigation of the long range transport of oxidants in the Kanto District and Nagano Prefecture of Japan. This is a particularly interesting study because it focuses on the impact of a major metropolitan area, Tokyo, on the air quality of an important resort, forestry, electronics, and recreation area located in a mountainous region some 150 - 200 km away. It is also of interest because the long range tranpsport mechanisms in Japan mainly arise due to locally-induced flow systems resulting from its geographic features, and not the symoptic scale pressure system affecting long range transport in North America. The STEM-II model and the Japan study are described in the following sections.

## II. Overview of the STEM-II Model

The STEM-II model (Carmichael et al., 1986) is an Eulerian combined transport/chemistry/removal model which treats chemical species in the gas, cloud, rain and snow phases. Thirty species are advected, while twenty-five species are short-lived and are modeled using pseudo-steady state methods. The advected species satisfy the folowing equations

Gas Phase:

$$\frac{\partial C_i}{\partial t} + \frac{\partial (U_j C_i)}{\partial x_j} = \frac{\partial}{\partial x_j}\left[K_{jj}\frac{\partial C_i}{\partial x_j}\right] + R_i + S_i + G_i \qquad i=1,\ldots,35 \qquad (1)$$

Cloud, Rain and Snow Phases:

$$\frac{\partial (S_m C_{im})}{\partial t} + \frac{\partial}{\partial x_j} (U_j - V_{sm}) S_m C_{im} = \frac{\partial}{\partial x_j} (K_{jjm} C_{im} \frac{\partial S_m}{\partial x_j} + R)_{im} + G_{im} \qquad (2)$$

$$i=1,\ldots,35 \quad m = 1 \text{ for cloud } (V_{sm}=0)$$
$$= 2 \text{ for rain}$$
$$= 3 \text{ for snow}$$

where $C_i$'s denote the concentrations,

$U_j$'s are velocity components,

S's are the liquid water contents,

$V_s$'s are the setting velocities of the hydrometeors,

$K_{jj}$'s are the eddy diffusivities, and

$R_i$, $G_i$ and $S_i$ are the rates of chemical reaction, mass transfer, and emissions, respectively.

The STEM-II model is structured to treat in detail wet removal processes. A schematic of the processes that are included in the model analysis is presented schematically in Figure 1. In this model, the in-cloud scavenging of sulfate aerosol is presumed to occur totally by nucleation. Both cloud and aerosol size distributions are assumed to be monodispersed. Once the cloud forms, the number of sulfate aerosols activated and dissolved to form aqueous sulfate is assumed to be the same as the number concentration of cloud droplets. Rain drops are also assumed to be monodispersed. Secondary sulfate is treated in the same way as primary sulfate and is allowed to be reinjected into the gas phase as hydrometeors evaporate.

The cloud parameters are calculated by the ASM cloud scavenging model (Hales, 1984). The ASM model treats the cloud microphysics and calculates the cloud and precipitation distributions, and interconversion rates. ASM calculates a self

consistent and realistic meteorological data set of the simulated storm. The precipitation-formation processes are treated in a parameterized fashion. The parameterizations of rain-formation are adapted from Berry and Reinhardt (1974), Scott (1982), Kessler (1969), and Lin et al., (1983). The snow-formation is parameterized based on schemes similar to that developed by Lin et al., (1983) and Scott (1982). The scheme lumps water into four categories: water vapor, cloud water, rain and snow. The cloud related parameters calculated in ASM are transferred to the STEM-II model where the transport/chemistry/removal of pollutants is calculated.

For the gas phase, the new reaction mechanism of Lurmann et al., (1986) for use in long range transport and acid deposition modeling, which includes 112 reactions and 55 chemical species, is used. Of these species, 35 long-lived species are advected while the remaining 25 short-lived species such as free radicals are modeled using Pseudo Steady State Approximation.

In addition, for the liquid phase, 16 dissociation expressions, 31 chemical reactions and 21 ionic species based on the work of Chameides et al., (1984) are included in the STEM-II code. Detailed solution equilibria and chemical kinetics are solved using a modified semi-implicit method while satisfying the electrical-neutrality constraint. Also, the mass transfer associated with absorption into, and desorption from droplets is included.

The effect of clouds on the solar flux values is also included in this analysis. The following empirical correlation relating photon flux to cloud cover (Kaiser and Hill, 1976) is employed.

$$F = F_c(1 - AC^{1.75}) \qquad (3)$$

where $F_C$ is the photon flux for clear sky, C is the cloud cover fraction, and A is a constant dependent on cloud type.

The numerical integration of the model equations makes use of the concept of fractional time steps and one-dimensional finite elements; referred to as the Locally One-Dimensional Finite Element Method (LOD-FEM). The transport equations are solved using a modified Galerkin FEM with asymmetric weighting functions and the Crank-Nicolson method for time. The chemistry equations are solved using a modification of the semi-implicit Eulerian method. Details of the numerics used in the model are found in Carmichael et al. (1986).

## III. Description of the Japan Study

The area of study is shown in Figure 2. The Central Mountainous Region of Japan consists of mountain chains 2,000 - 3,000 m high with a complex terrain consisting of many basins and valleys. The average height of this region is ~ 1200 m MSL. The area is only ~ 150 - 200 km from Tokyo and is one of the premier summer and winter resort areas. The area has traditionally had a strong forest industry. In the last decade or so the area has experienced significant industrial growth with many microelectronics companies moving manufacturing facilities from the more polluted area along the Pacific Ocean coast of Japan to the cleaner environs of Nagano Prefecture. However, in the summer high concentrations of photochemical oxidants (OX) are frequently observed at inland stations in the Central Mountainous Regions. For example, the cities of Ueda and Nagano are located in the central mountainous region of Japan more than 160 km from large-scale emission sources of the Toyko area. Ueda ranked seventh in Japan in 1979 for the number of days on which more than 120 ppb of OX was recorded. Furthermore, the daily

maximum OX concentration in this region occurs in the late evening, mostly around 1900 JST (henceforth all times are JST at Ueda and midnight at Nagano). Such a high nighttime concentration is the most remarkable feature of air pollution at these stations. Moreover, these high concentrations of OX occur on clear days with light gradient winds under synoptic-scale high pressure systems. These observations are indicative of the long-range transport of photochemical smog.

To understand the long range transport of OX to the Central Mountainous Region a large field study was organized. The area studied is shown in Figure 2. An outstanding meteorological and chemistry data set has been collected during 2 campaigns in the summer of 1983 and 1984. The meteorological data consists of surface winds collected from the Automated Meteorological Data Acquisition System (AMeDAS) every hour. There are around 200 stations in this region. During the intensive measurement periods, the upper wind data were taken at 16 stations located along the route of the polluted masses using Pilot balloon, Kite balloon, and radiosonde. In addition there were 7 intensive pollutant monitoring sites which measured NO, $NO_2$ and $O_3$, sulfate, $SO_2$, nitrate, nitric acid, TSP, $NH_4^+$, and 30 hydrocarbon species. These $O_3$ measurements were augumented by aircraft and an instrumented van. The location of the chemistry sites are shown in Figure 1. Their locations were chosen based on the extensive meteorological and $O_3$ climatology analysis of the region.

The meteorological mechanism of long range transport of OX to Nagano Prefecture has been carefully studied and reported recently by Kurita et. al., (1985 and 1986). The mechanism includes light gradient winds, thermal in the Central Mountainous Region, extended sea breeze flows, and valley winds. The typical trajectory of the

air mass is shown in Figure 2 by the dotted line. The topography along this trajectory is also shown. At the Usui Pass region the width of the pass is less than one kilometer, with the valley surrounded by 2-3 km MSL ridges. Depending on the location of the convergence line the polluted air masses from the Tokyo area will either be blocked by the pass or will penetrate over the pass.

The STEM-II model is being used to help analyze these data. Currently we are focusing on OX transport on July 29-30, 1983. This period was a case where the polluted air penetrated over the Usui Pass and high OX levels were observed in Karuizawa. Currently a 2-dimensional version of the model is used with the model region selected along the dotted line in Figure 2. A series of 3-d inert trajectories were calculated and show that the trajectories cluster around this path (see Figure 3).

The 2-dimensional domain and model grid system is shown in Figure 4. The domain stretches from Ohshima Island (include to account for ship emissions in the harbor) in the Tokyo Bay to beyond Nagano City. The 2-d flow field is obtained using objective analysis based on a variational method for minimizing of the divergence (Kitada et al., 1983) and is shown in Figure 5. The flow field at 12:00 shows the extended sea breeze front, the valley winds around Usui Pass and the convergence line resting near Karuizawa. At later times the convergence line shifts to the Northwest to near Ueda. Inert trajectories are shown in Figure 6 for particles released at 12:00. As indicated, particles released near the surface are blocked by the mountains and do not pass elevations higher than ~0.5 km. Particles released at 200 m penetrate over the Usui Pass then stagnate at about 1 km over Ueda. Particles at 600 m penetrate over the pass then are transported to the SE by the return flow.

$O_3$ Predictions:

The strong emission regions are in the industrial and highly populated areas around Yokohoma, Tokyo, and Urawa. The emissions of selected species are shown in Figure 7. The emissions are characterized by extremely high $NO_x$ and hydrocarbon emissions in the Tokyo area.

The predicted and measured ground-level $O_3$ values are presented in Figure 8. The predicted values are in excellent agreement with the observations. The $O_3$ values in the highly polluted regions of Yokohama and Tokyo show a typical diurnal variation with maximum $O_3$ forming in the early afternoon. About 50 ppb of $O_3$ is found in the urban area of Yokohama. The $O_3$ values in Tokyo show the same diurnal trends with lower $O_3$ values reflecting the higher $NO_x$ emissions in this region. At Urawa the concentration of $O_3$ shows the same diurnal trend but with $O_3$ values near 100 ppb. These levels are due to the polluted air mass from Toyko combining with local emissions. The transport of the polluted air mass can be seen in the $O_3$ values of Takasaki and Karuizawa. The $O_3$ values at Takesaki reach ~ 150 ppb at 16:00. The polluted air mass reaches Karuizawa at 18:00. Shown in the predicted profile at Karuizawa are the local $O_3$ production of 30 ppb at ~ 12:00 and a peak due to long range transport at 18:00 of ~ 150 ppb. The general movement of the $O_3$ polluted air mass can be clearly seen in Figure 9 where the ground level $O_3$ values are plotted on the same figure.

Additional features of the transport and chemistry can be seen by examining the vertical structure of the predicted $O_3$ values (Figure 10). The predicted results clearly show the polluted air mass passing over Usui Pass, stagnating, and then rising and convected back to the SE by the return flow. These features are in good agreement with the observations.

The calculated total dry deposition flux of $O_3$ for the 27 hour period is shown in Figure 11. These results are obtained using a spatially and temporally constant deposition velocity for $O_3$. The results indicate that the total maximum surface exposure to $O_3$ occurs in the area around Takesaki and on the eastern slope of the mountain pass.

## IV. Closure

The Japan Study provides an important, unique and comprehensive data set which documents the meteorological and chemical features of long range pollutant transport in complex terrain. The data shows clearly that sources located 150-200 km from the region can have a profound impact on the local air quality. The STEM-II model is being used to help analyze this data set and the preliminary results show that the model predictions are in excellent agreement with the observations. The model is now being used to quantify the important chemical mechanisms, to calculate deposition rates, and to evaluate various source control strategies.

The results (predictions and observations) show that the polluted air mass from the Kanto Plain frequently impacts the mountainous region located ~ 150-200 km from Tokyo, and often times penetrates over the Usui Pass into the Nagano area. There is currently concern regarding the impact of this long range transport of pollutants on the forest, microelectronics and recreational industries located in the central mountainous region. The concern is compounded by the fact that low lying clouds frequently form on top of Usui Pass. We are currently analyzing (both data and model analysis) the cloud chemistry in this region.

The STEM-II model is also being used to analyze other meso- and regional-scale pollutant transport studies. Three

dimensional model analysis in cooperation with EPA, NASA, MESO, Inc. and BNL is being used to investigate the impact of urban emissions on wet deposition. Diagnostic analysis of field study data is being conducted to identify the important chemical mechanisms of oxidant and acid formation, and to calculate the amount of the local emissions which escape from the meso-scale area and thus become available for long range transport. Three-dimensional analysis of STEM-II is also being done to analyze field data and the effect of various source scenarios on pollutant transport and formation in the eastern United States during precipitation events. This is being done in conjunction with the DOE PRECIP program.

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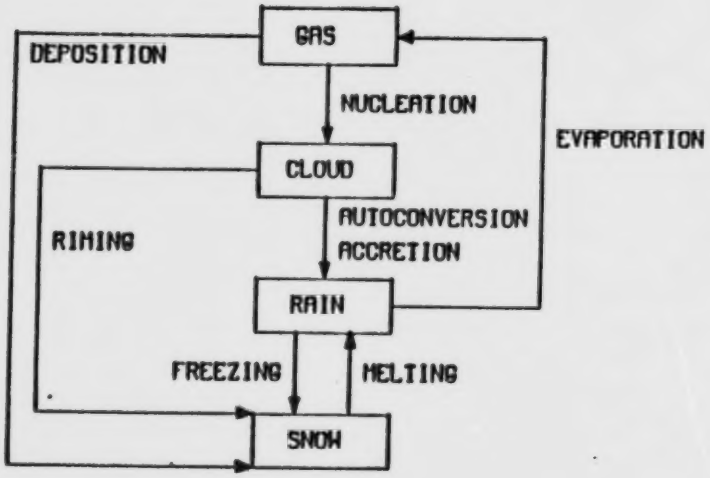
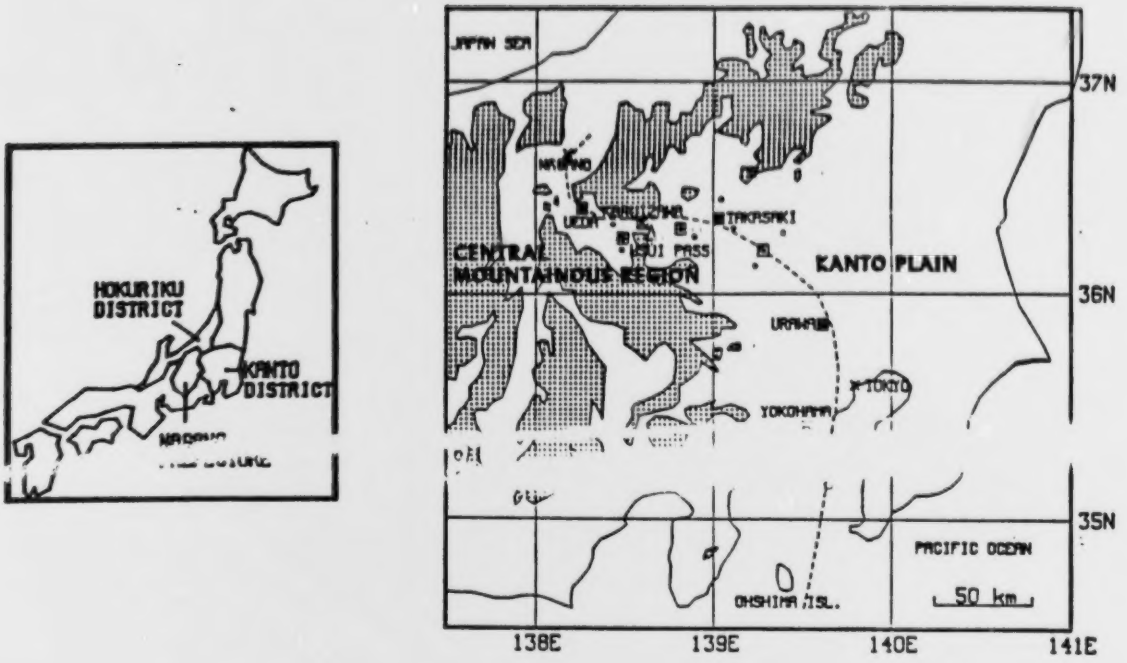



Figure 1 Schematic diagram of chemical and physical processes treated in the STEM-II model.



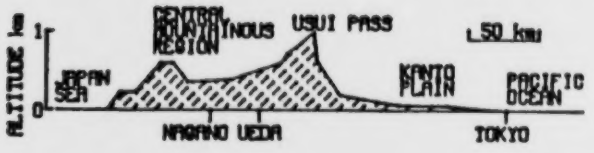




Figure 2 Geographical features of the area analyzed; land higher than 1000 m MSL is denoted by stippled area; the dotted line represents the path of pollutant transported. Pollutant measurement-sites are denoted by x, pibal measurement sites denoted by o, kite balloon measurement sites denoted by □, and radiosonde sites denoted by +.

# TRAJECTORIES

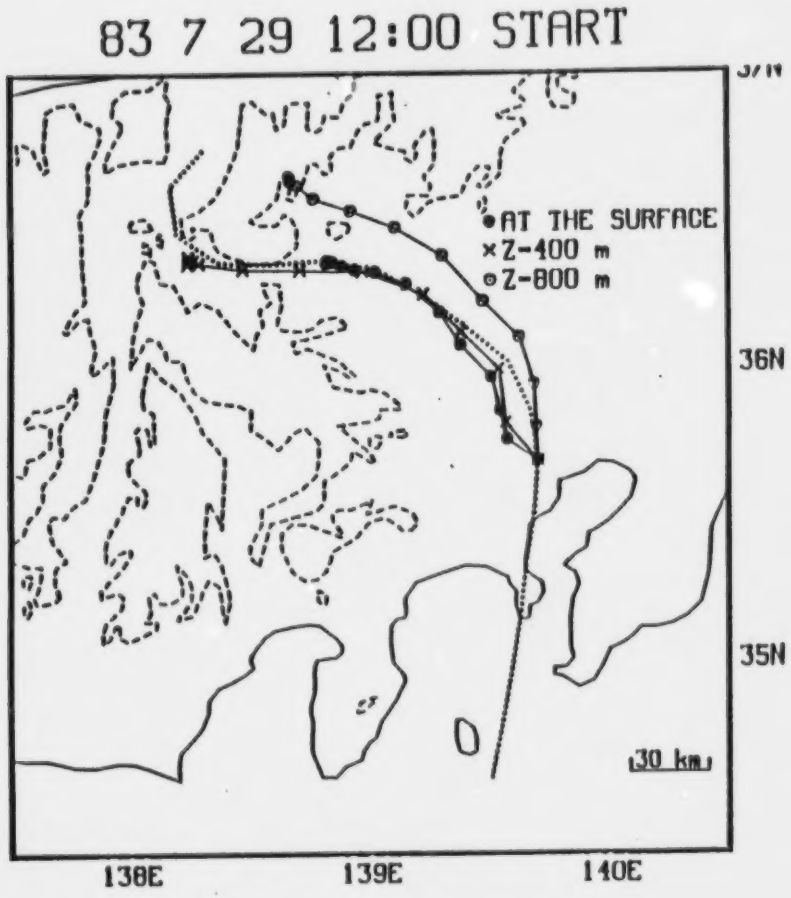



Figure 3 Computed movements of hypothetical particles released near Tokyo at 1200 JST, July 29, 1983.

# MODEL GRID SYSTEM

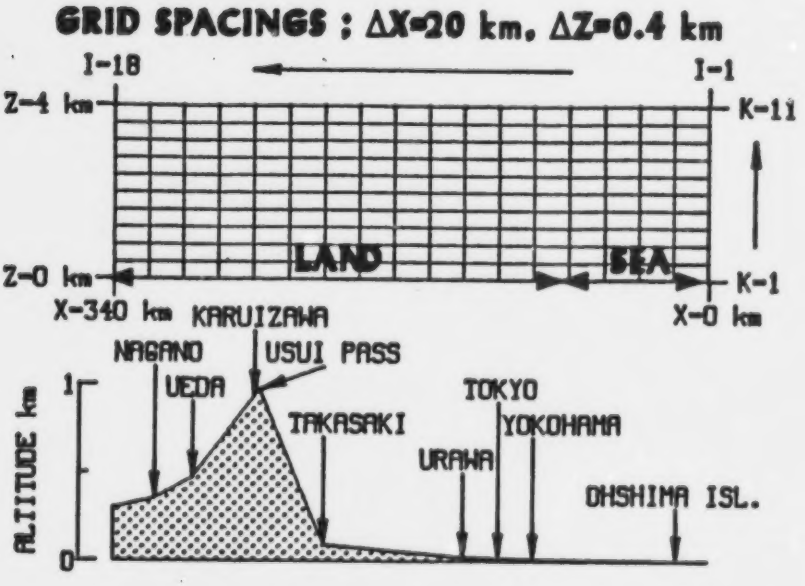



Figure 4 The 2-Dimensional domain and model grid system.

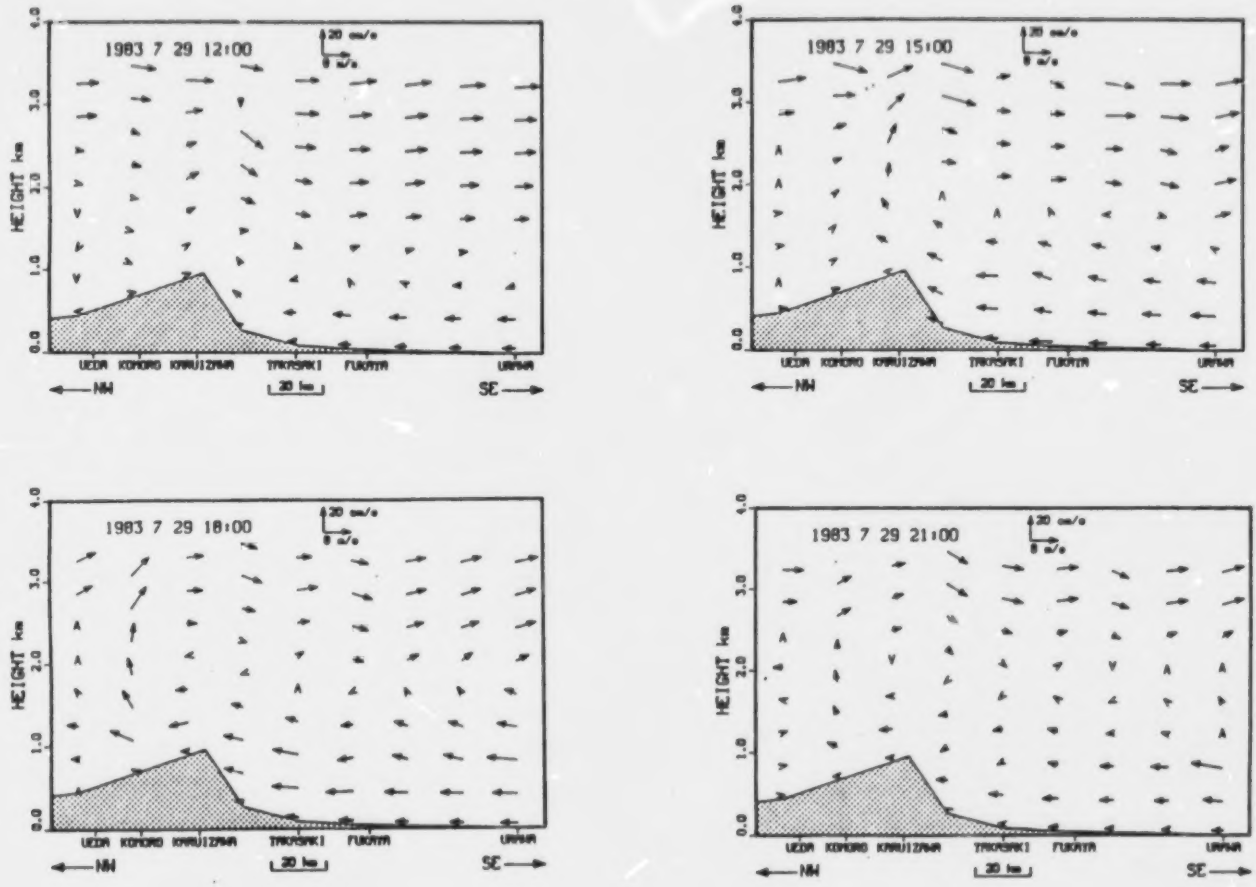



Figure 5 The 2-Dimensional wind field: (a) 1200, (b) 1500, (c) 1800, (d) 2100 JST, July 29, 1983.

# TRAJECTORIES

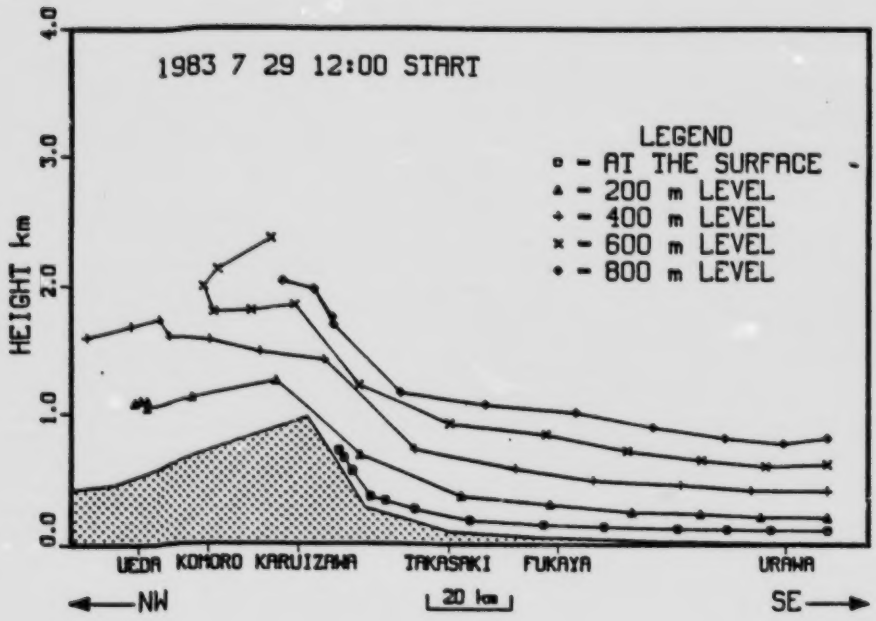



Figure 6 The 2-Dimensional trajectories of hypothetical particles released near Tokyo at 1200 JST, July 29, 1983.

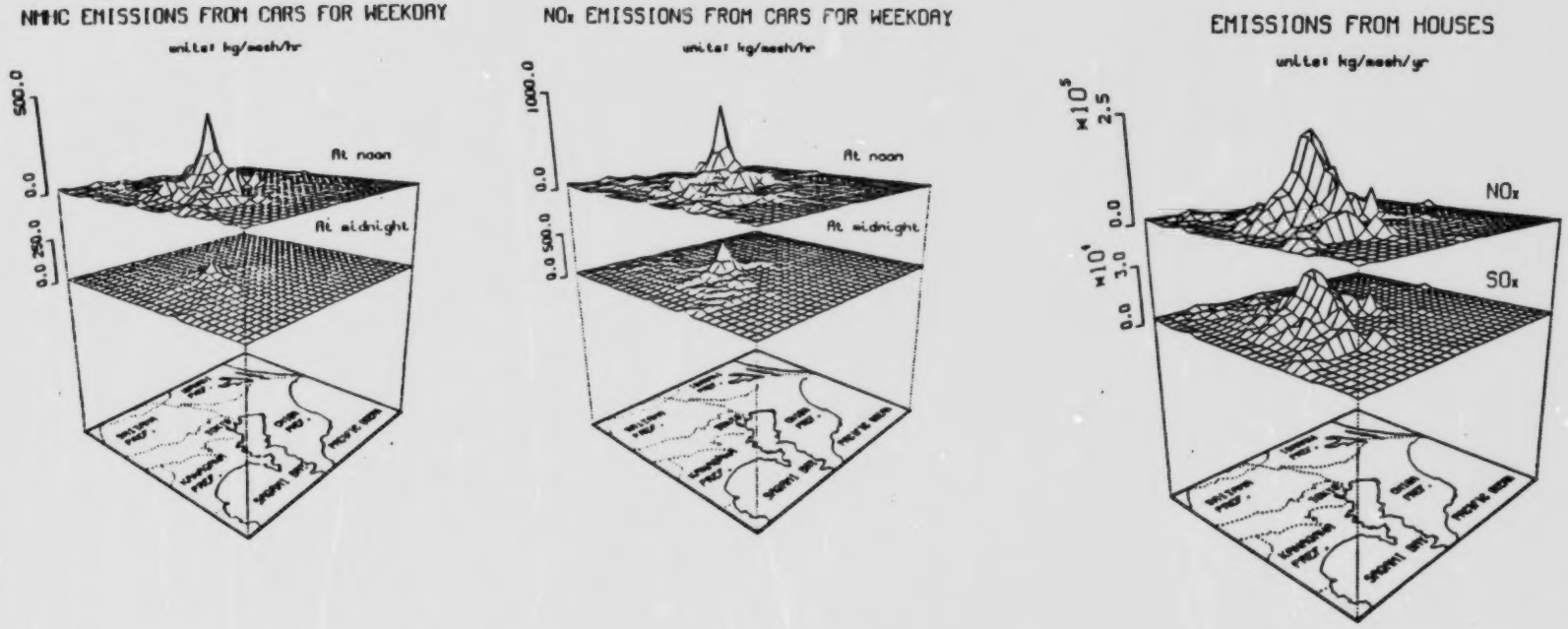



Figure 7 Emission fields: residential source, $NO_x$ mobile source, NMHC mobile source.

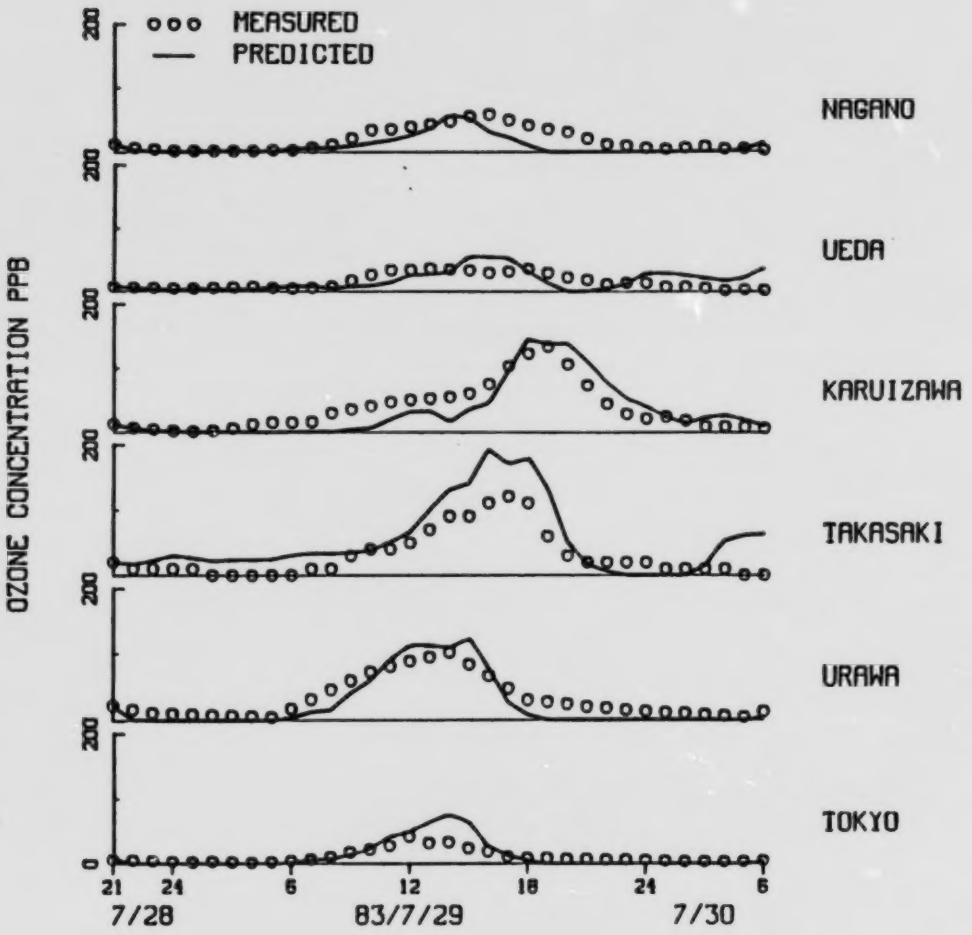



Figure 8 Comparison between measured and predicted values of $O_3$.

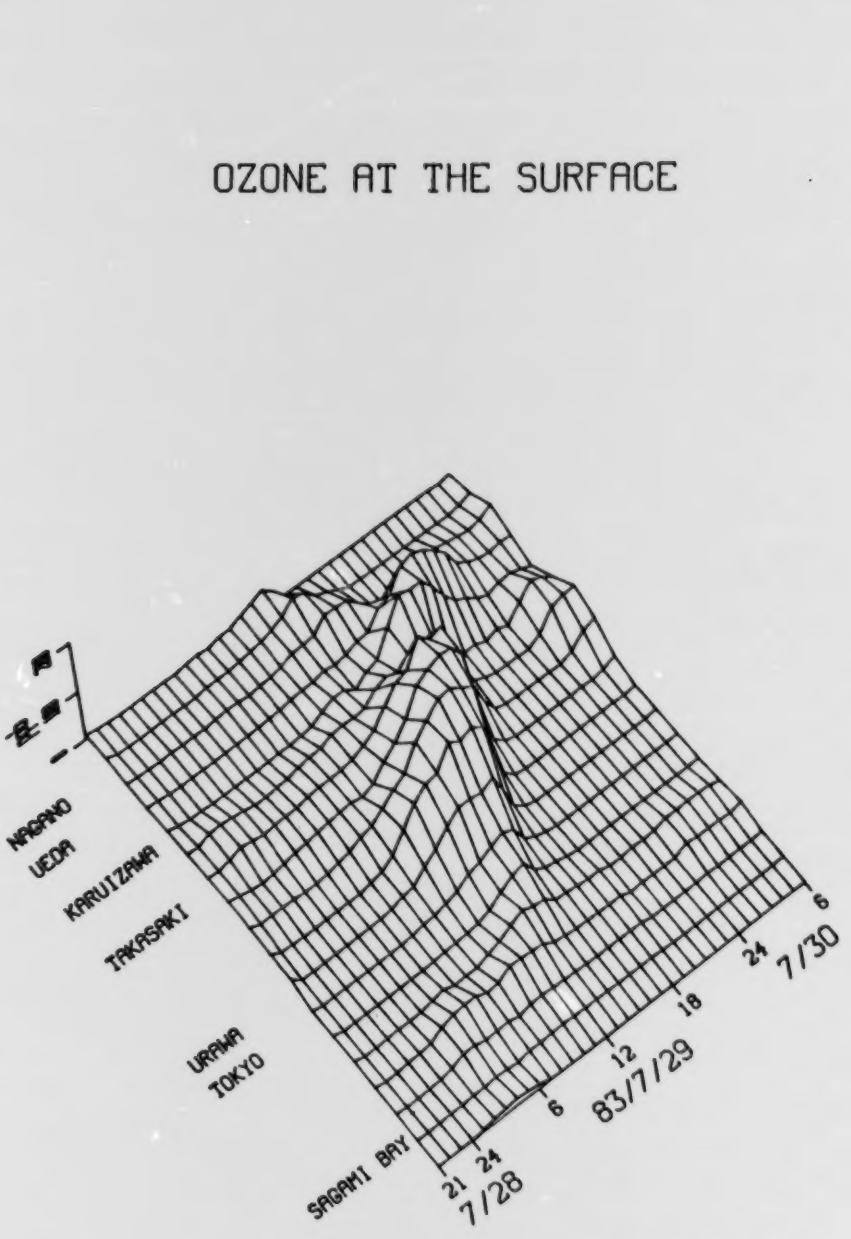



Figure 9 Predicted $O_3$ movement at the ground level.

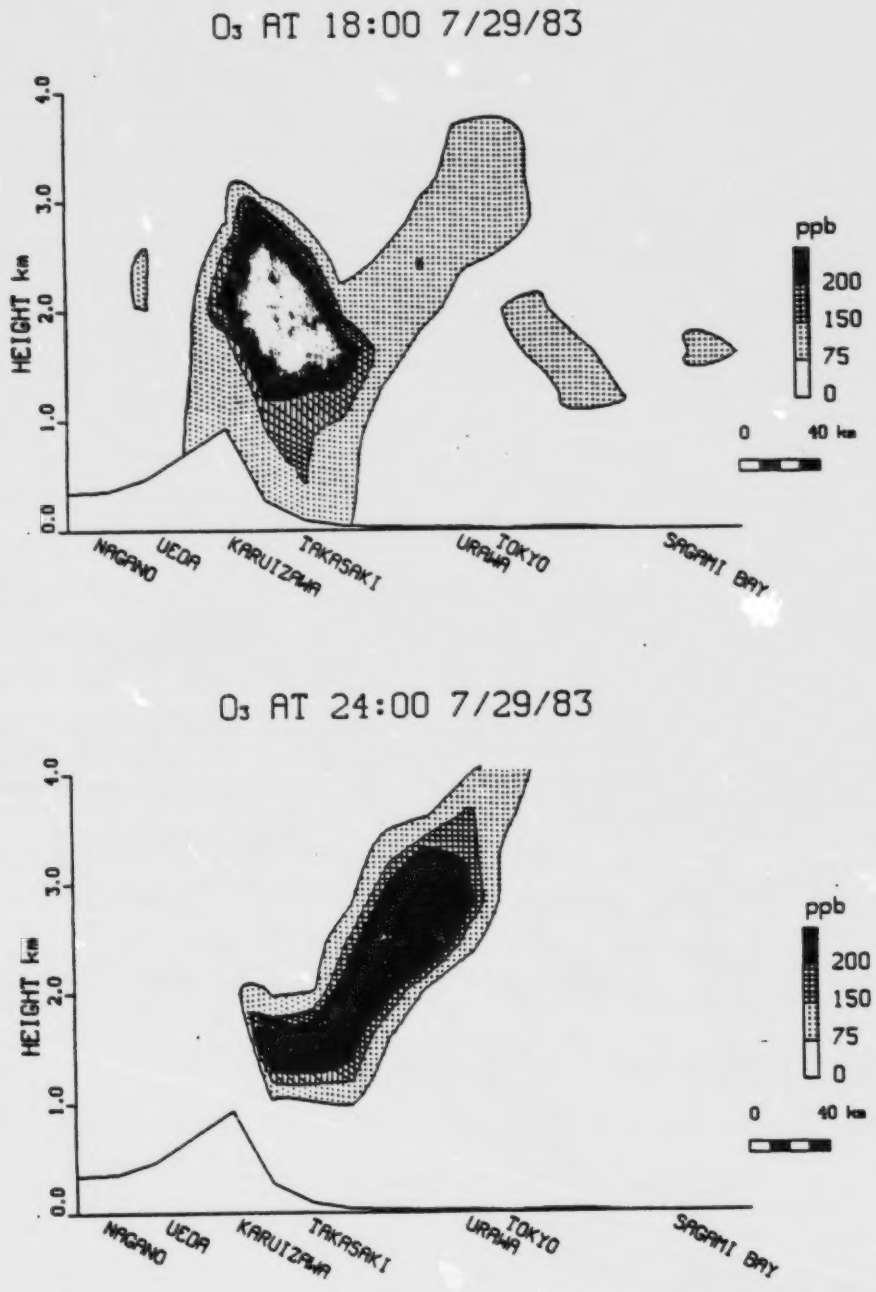



Figure 10 Predicted vertical $O_3$ movement: (a) 1800, (b) 2400, JST, July 29, 1983.

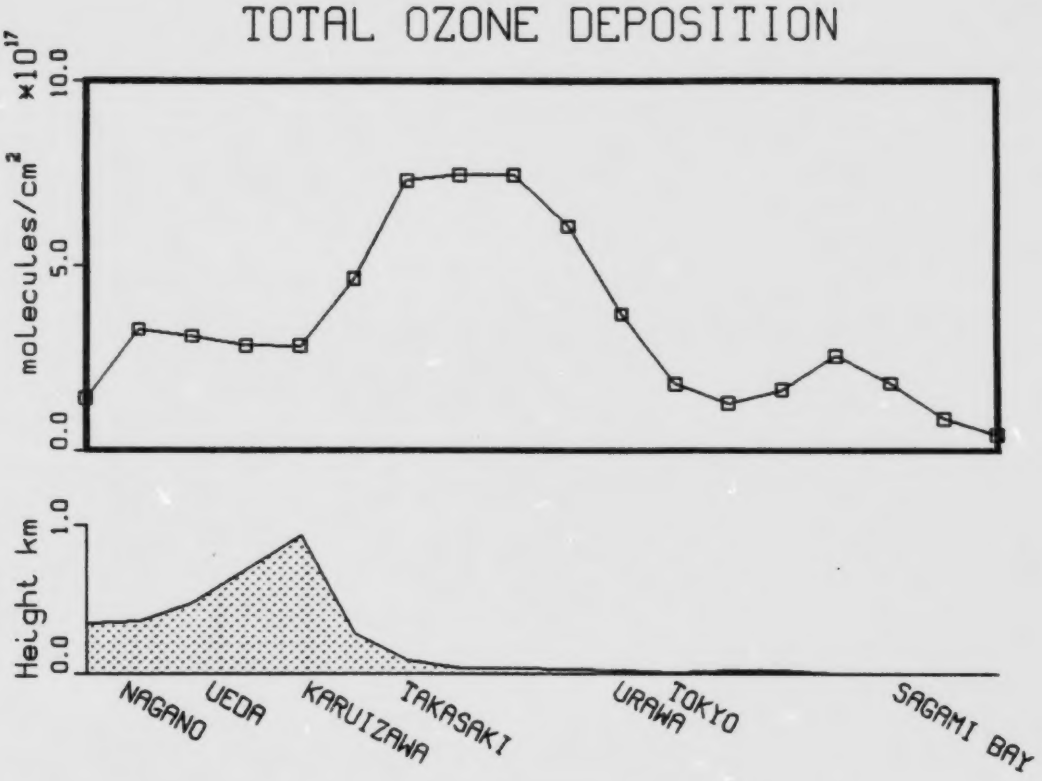



Figure 11 Total integrated surface deposition of $O_3$ as a function of position.

# ASSESSMENT OF THE OZONE PROBLEM IN THE NEW YORK METROPOLITAN AREA

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## RÉSUMÉ

Le présent exposé présente les résultats de simulations réalisées à partir du modèle de bassin d'air urbain pour cinq journées à fortes concentrations en ozone dans la région métropolitaine de New York. Diverses techniques d'analyse statistique appliquées aux données sur les concentrations d'ozone prévues et observées révèlent que les prédictions du modèle sur les concentrations d'ozone dans la région métropolitaine de New York sont comparables à celles obtenues avec ce même modèle dans d'autres villes. À l'aide du modèle, on a ensuite examiné l'incidence de stratégies précises de réduction des émissions sur la qualité de l'air ambiant de cette région. Les résultats indiquent que même l'application des mesures de réduction convenues dans le cadre des State Implementation Plans en matière de modélisation et dans les régions exposées au vent ne suffirait pas à ramener les taux d'émissions sous ceux prévus par les normes nationales sur la qualité de l'air ambiant pour la saison 1988.

## ABSTRACT

This paper presents the results of the Urban AIRSHED Model (UAM) simulations for five high ozone days in the New York Metropolitan area. Various statistical analysis techniques applied to the measured and predicted ozone concentration data reveal that the UAM performance in predicting the ozone concentration values in the New York Metropolitan area is comparable to the results of previous evaluations of UAM in other cities. The UAM was then applied to examine the impact of selected emissions control strategy options on the ambient air quality in this region. The results indicate that even with the implementation of control measures committed to in the current State Implementation Plans (SIPs) of the states in the modeling domain and in the upwind regions, peak ozone concentrations in the New York Metropolitan area would not be reduced to levels below that of the ozone National Ambient Air Quality Standard in the 1988 oxidant season.

## 1. INTRODUCTION

Pursuant to the Clean Air Act (CAA), the U.S. Environmental Protection Agency (USEPA) has promulgated primary and secondary National Ambient Air Quality Standards (NAAQS) for photochemical oxidant. The NAAQS will be attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is equal to or less than 1. Section 110 of CAA requires that State and local air pollution control agencies identify methods in their State Implementation Plans (SIPs) which will reduce precursor emissions in urban areas to the extent necessary to comply with the NAAQS. Since implementation of a control strategy may require significant economic commitments and may cause severe social dislocation, reliable estimates of ozone concentrations due to the impact of precursor emissions from a specific urban area must be available prior to making a decision to adopt a particular control strategy for the area.

Ozone levels downwind of an urban area can be related to a specific area's precursor emissions and transported ozone and precursor concentrations by photochemical simulation models. Such models provide a tool for estimating the impact of alternative control strategies on ozone concentrations. Confidence can be placed in the impact evaluation process only if reliable ozone prediction relationships are employed. Numerical photochemical transport and dispersion models such as the Urban AIRSHED Model, UAM, (Ames, et al., 1985a) and Livermore Regional Air Quality Model, LIRAQ, (McCraken, et al., 1975) are among the most sophisticated of the approaches, and are state-of-the-art models for predicting the spatial and temporal distributions of ozone concentrations downwind of urban areas. Although this is perhaps the best approach in theory, numerous problems arise in practice. These include difficulties with several features of this urban modeling approach such as 1) in numerically solving the complex conservation of

mass equations accurately, 2) the high computational costs, 3) the high level of technical expertise required for model implementation and interpretation, 4) the unknown effects of the limitations of available data for specifying the treatment of transport, diffusion and chemical reaction processes, 5) the large data requirements for testing the critical features of the model, and perhaps, more importantly, 6) the need for a spatially and temporally accurate emissions inventory.

The objectives of this study were to assess and quantify the ozone problem in the New York Metropolitan area, and to evaluate the available control options for developing effective and equitable strategies to reduce the ozone levels in the region. The UAM was selected as the photochemical oxidant model for use in this study. The New York Metropolitan area included in the modeling domain consists of portions of New Jersey, New York and Connecticut. Based on an assessment of the meteorological conditions and ambient air quality data during the summer of 1980, five high ozone days were selected for detailed modeling analysis (see NYSDEC, 1987 for details). The pertinent emissions, meteorological, and air quality data were assembled to execute the UAM for these days for the 1980 base year. The predictions were compared with ambient measurements from monitoring stations in the three states to evaluate the model performance. To evaluate the impact of selected control options, a projection of the 1980 base year emissions to a 1988 emissions scenario was prepared based on information in the approved 1982 SIPs. Using this inventory and the meteorological conditions observed in 1980, model simulations were performed to assess the impact of selected emissions reduction strategies on ozone concentrations. The modeling results revealed that even with the full implementation of control measures committed to in the current SIPs, ozone levels in the 1988 oxidant season for the New York Metropolitan area would be well above the ozone NAAQS.

## 2. Base Year Simulations

The areal extent of the modeling region selected in this study was guided by the primary objective of capturing the peak ozone concentrations resulting from the emissions in New Jersey, New York, and Connecticut. The modeling domain is shown in Figure 1. The region, covering an area of $49.6 \times 10^3$ $km^2$, is divided into a 8 km by 8 km cell in the east-west(x) and north-south(y) directions, yielding 31 cells in x and 25 cells in y direction, respectively. The number of levels in the vertical(z) direction was set to four with three levels in the layer between the ground and the mixing height, and one level between the mixing height and the top of the modeling region. The thickness of each of these four levels was dependent upon the hourly mixing height with a minimum height of 50 m for the layers below the mixing depth and 500 m for the layer between the mixing height and top of the region.

By virtue of its design, the UAM requires the input of various aerometric data sets, shown schematically in Figure 2, for simulating the concentration field (Ames, et al., 1985a, 1985b). In a majority of the applications, the required input data are not available from routine measurements and have to be developed from special monitoring networks. One such network is the 1980 Northeast Corridor Regional Modeling Project (NECRMP, 1982) conducted by USEPA, which provided a detailed and extensive aerometric data base for this region. Examination of this data base led to the selection of five high ozone days which consisted of ozone levels exceeding 200 ppb in portions of the modeling domain. The five days selected were JD80198(071680), JD80203(072180), JD80204(072280), JD80219(080680), and JD80221(080880). The synoptic weather pattern associated with those days included a frontal array across the northeast U.S-Canada border, slightly disturbed westsouthwesterly to westnorthwesterly flow aloft in the northeast, a weak surface trough east of the Appalachians, and a

Figure 1: The ONEYMAP Modeling Domain

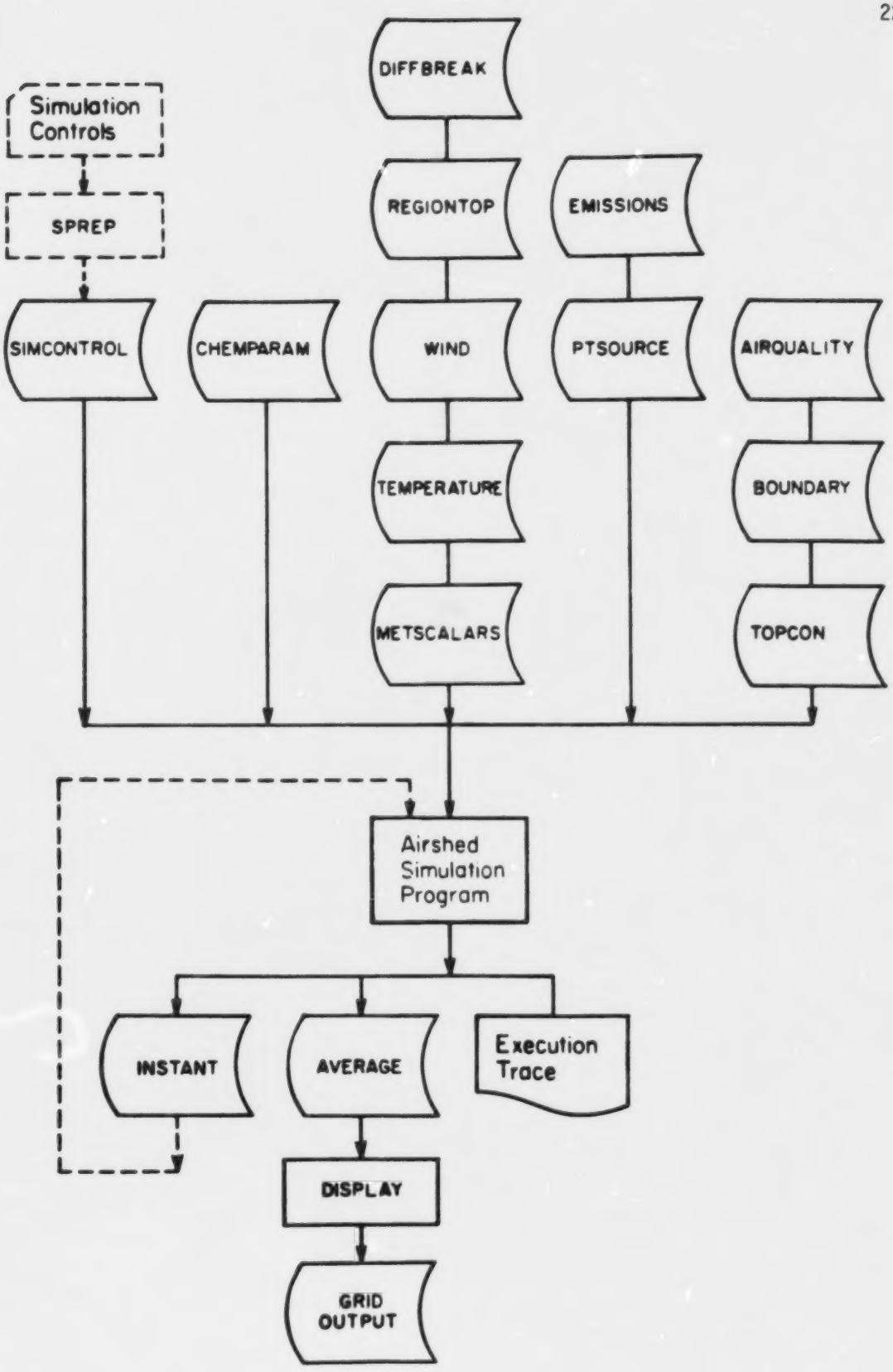



Figure 2: The SAI - Urban Airshed Model Flow Chart

surface high pressure system over the Atlantic extending westward through the southern states. These conditions were found to be typical of other high ozone days in the New York Metropolitan area.

## 2.1 Model Input Parameters

### 2.1.1 Meteorological and Air Quality Conditions

The meteorological parameters needed to execute the UAM are provided in Table I. The following is a brief description of the methodologies employed in obtaining these parameters. Further details on the procedures for preparing the input data files for the UAM can be found in NYSDEC (1987).

Diffusion Break (Mixing Height): The available data for the delineation of the mixing heights included rawinsonde temperature soundings and vertical profiles of temperature and pollutant concentrations as measured by instrumented aircraft. Mixing heights were calculated using these data following the methods of Benkley and Schulman (1979), Nieuwstadt (1981) and Garrett (1981).

Modeling Region Top: A variable region top height which rises at a rate slower than the mixing height in the morning hours was selected. The region top and mixing height become equal by mid-day. Figure 3 shows an example of the diurnal profile of the top of the modeling region and mixing height over the domain.

Surface Temperature: The distribution of the surface temperature over the modeling domain was derived through an inverse-distance-squared weighting interpolation scheme utilizing the National Weather Service (NWS) measurements for each hour of the model simulation.

TABLE I

Meteorological Parameters Required for the Urban Airshed Model and Their Variation in Space and Time

| Parameter | Variability | |
|---|---|---|
| | Space | Time |
| Diffusion break (mixing height) | x, y | t |
| Top of the modeling region | x, y | t |
| Surface temperature | x, y | t |
| Atmospheric pressure | | t |
| Concentration of water vapor | | t |
| Exposure Index | | t |
| $NO_2$ Photolysis Rate constant | | t |
| Temperature gradient above and below the diffusion break | | t |
| Wind field in terms of u and v | x, y, z | t |

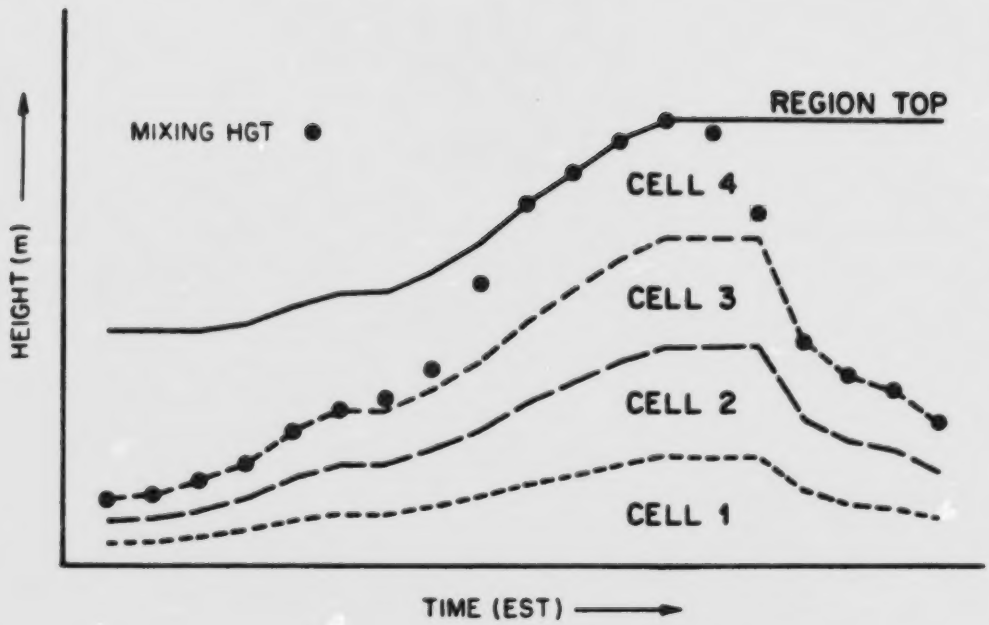



Figure 3: Schematic Diurnal Profile of the Region Top, Mixing Height and Vertical Cell(s) Height

Atmospheric Pressure: Sea-level atmospheric pressure values obtained from the NWS stations for each hour were averaged to yield a single value for the domain for each hour simulated.

Concentration of Water Vapor: Following Byers (1971) and Hull (1974) the specific humidity at saturation, $q_s$, was obtained as follows:

$$q_s \text{ (grams of } H_2O\text{/grams of air)} = 0.622\ e_s/(P-0.37\ e_s)$$

where $e_s$, the saturation vapor pressure (mb), is given by

$$e_s = E_s \exp(AT/X)$$

where
$X = (T + 273.16-B)$
$A = 17.2693882$
$B = 35.86$
$E_s = 6.1078$
$P$ = Atmospheric Pressure (mb)
$T$ = Dew Point Temperature (°C)

In this study, the specific humidity at saturation for each hour was calculated from the data collected at the NWS station at JFK Airport in New York City, which was then multiplied by $10^6$ to yield the water vapor concentration in ppm and used as a representative value for the domain.

Exposure Index: This parameter which is a measure of near ground level stability due to surface heating or cooling was estimated from insolation. Solar radiation data from Flemington and Marlboro sites in the southwestern part of New Jersey and the hourly sky cover conditions reported from the NWS stations as well as synoptic weather information were used to estimate the exposure index for each hour.

Diurnal Photolysis Rate Constant: A computer program that incorporates the data of Demerjian, et al., (1980) was used to calculate layer-averaged $NO_2$ photolysis rate constants based upon the latitude, longitude, month, day and time of the day, mixing height, and solar radiation data. Utilizing the mixing height information and assuming clear sky conditions, the layer-averaged $NO_2$ photolysis rate constants were obtained for the modeling domain.

Temperature Gradient: The temperature gradients above and below the diffusion break (mixing height) were calculated from temperature soundings available at several locations in the modeling domain. The gradients for each hour were estimated by averaging the measured profiles at increments of 100m. For those hours for which data were not available, the gradients were obtained through linear interpolation.

Wind Field: The UAM program requires the specification of a three-dimensional flow field in a gridded form. Attempts were made to generate an interpolated gridded wind field based upon the available surface and upper air data using the Clark and Eskridge (1977) non-divergent algorithm. However, the representativeness of the upper air observations available at Marlboro, NJ or Glen Cove, NY, for the entire modeling domain was found questionable because of the influence of land-sea breeze circulations. Application of a bi-cubic splines interpolation technique to the surface wind observations for generating the wind field over the domain produced too much smoothing in the derived wind field. It was decided to use only the surface based observations and generate a two-dimensional non-divergent gridded wind field, assumed to be invariant in the vertical direction. However, examination of such a wind field and trajectory paths revealed the undue influence from the coastal NWS stations which appear to be affected significantly by the land-sea breeze interaction. Hence, a

spatially constant but temporally varying vector-averaged wind field for each hour of the simulation was considered to be a reasonable approach for capturing the transport characteristics prevailing in the modeling domain.

Initial Conditions for Pollutant Concentrations: The following procedures were adopted to obtain the gridded pollutant distribution at the surface and in the vertical. For each of the pollutants the concentrations measured at the ambient monitoring stations for 0300 and 0400 hrs were averaged to generate gridded surface concentrations. For ozone the method was based upon an inverse-distance-squared weighting scheme. In the case of the precursors, it was based upon the population distribution which was used as a surrogate parameter since there were very few surface stations from which data were available to make a meaningful interpolation over the modeling domain.

Based upon the pollutant measurements made by aircraft over the domain, the initial concentrations at the top of the modeling domain and in vertical layer 4 for each of the pollutants were estimated. For the intermediate levels between the surface and the base of the vertical layer 4, a linear interpolation scheme was employed to determine the pollutant concentrations with the assumption that the concentrations are uniform from the ground up to the base of vertical layer 4 for those grids that are classified as urban. In the case of grids that were considered rural, the pollutants were assumed to follow the same gradient as determined from the aircraft data. This is shown schematically in Figure 4.

Boundary Concentrations: The surface concentrations along the boundaries for each hour were estimated based upon the monitoring stations located outside the modeling domain. Attempts were made to take into account the wind direction for each hour in arriving at the surface

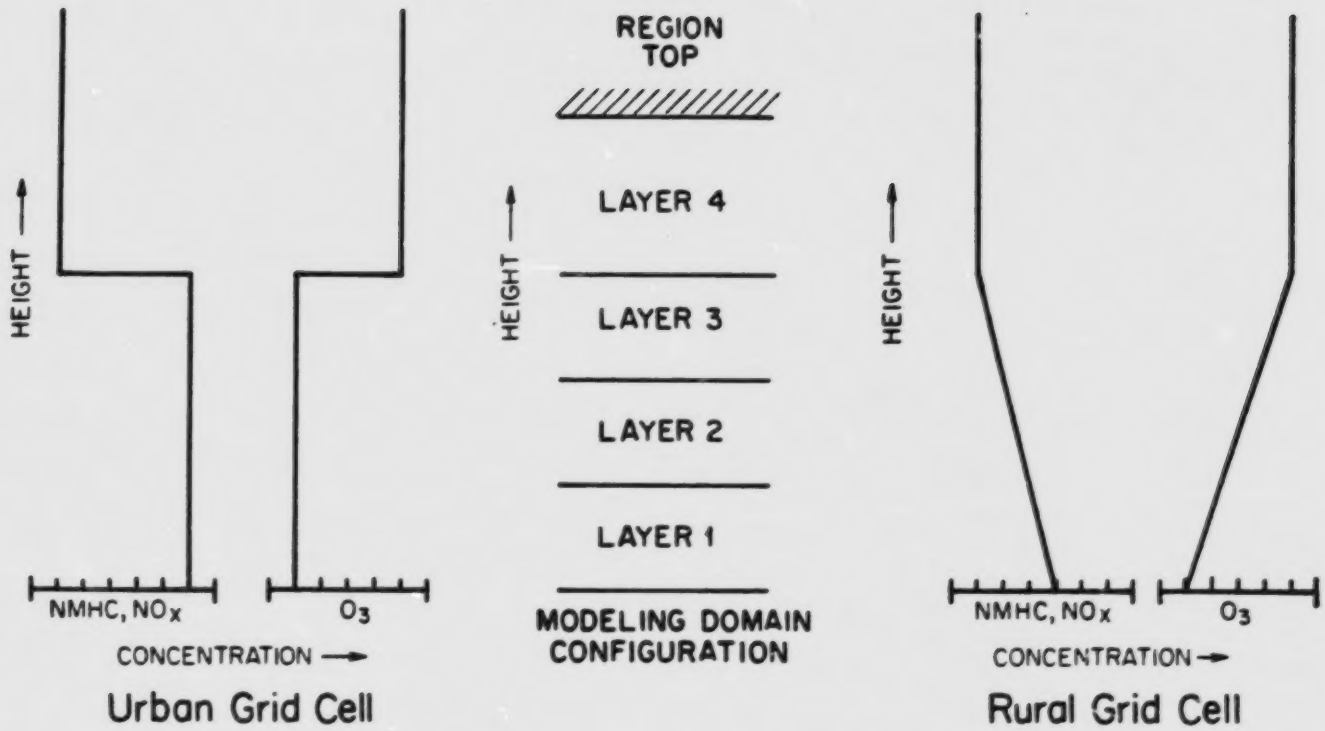



**Figure 4: Schematic Distribution of Initial Pollutant Distribution in the Vertical Plane for Urban and Rural Grid Cells**

boundary concentration based upon the location of the monitoring station and availability of data. The vertical gradients of the pollutants determined from the aircraft measurements were applied to all four sides and used to determine the concentrations in the vertical up to the 3rd layer. In the case of the 4th layer and the top of the region, pollutant concentrations were estimated as the average from aircraft measurements at that altitude. This procedure was adopted for those hours for which the diffusion break (mixing height) was at or below the vertical layer 4 or until the occurrence of inversion breakup. For all subsequent hours, the pollutants were considered to be well-mixed throughout the layer from the surface up through the 3rd layer.

### 2.1.2 Emissions Inventories

UAM requires an emissions inventory for each hour by grid cell (8 km x 8 km) in terms of the CO, $NO_x$, and hydrocarbon components specified in the Carbon Bond II chemical mechanism.

Each state covered by the modeling domain has a different emission inventory system. Merging these data sets required the development of a new data management system which could accept emissions data in the format used by the National Emission Data System (NEDS). This system of computer programs makes use of modules from the Emissions Inventory System (EIS), which provides emission calculation procedures. These procedures allow a user to estimate emissions using process rates or activity levels and emission factors. The emission factors are stored in a user-maintained table which is arranged by source classification code (SCC) and pollutant identification number. The installed system provides the means to disaggregate annual emission estimates to an hourly basis using specific or typical operating schedules, and to speciate total hydrocarbons into several classes

depending on the composition of emissions from the source category. After performing these calculations, the system formats the data to the specifications of the UAM.

The new system designed can process four types of emission sources: major point sources, minor point sources, area sources, and mobile sources. Major and minor point sources are sources which emit significant amounts of pollutants from smokestacks or other readily identifiable emission points and for which detailed operating data are available. For this study, major point sources were defined as those with annual emissions greater than 100 tons and a stack height greater than 65 meters; all others are classified as minor point sources. Area sources are those such as residential sources which are too small and too numerous to handle individually. Mobile sources are generally considered to be motor vehicles on established roadways. The flow of the data through the new data management system is shown schematically in Figure 5.

In this study, the data bases were obtained from each of the three participating State agencies which were responsible for collecting and preparing data in a format that could be utilized by the emissions pre-processor programs. Based on the methodology described above, the 1980 base year VOC and $NO_x$ emissions were generated and are listed in Table II for each of the three states and for the entire modeling domain. Also listed in Table II are the projected 1988 emissions based upon the 1982 SIPs submitted by the three states. These data show an overall reduction of 32% in VOC and 14% in $NO_x$ from the 1980 base year across the modeling domain, although the level of reduction varies spatially by grid cell within each State. On a percentage basis, the VOC and $NO_x$ emissions for the base year are approximately 39% and 41% from New York, 40% and 41% from New Jersey

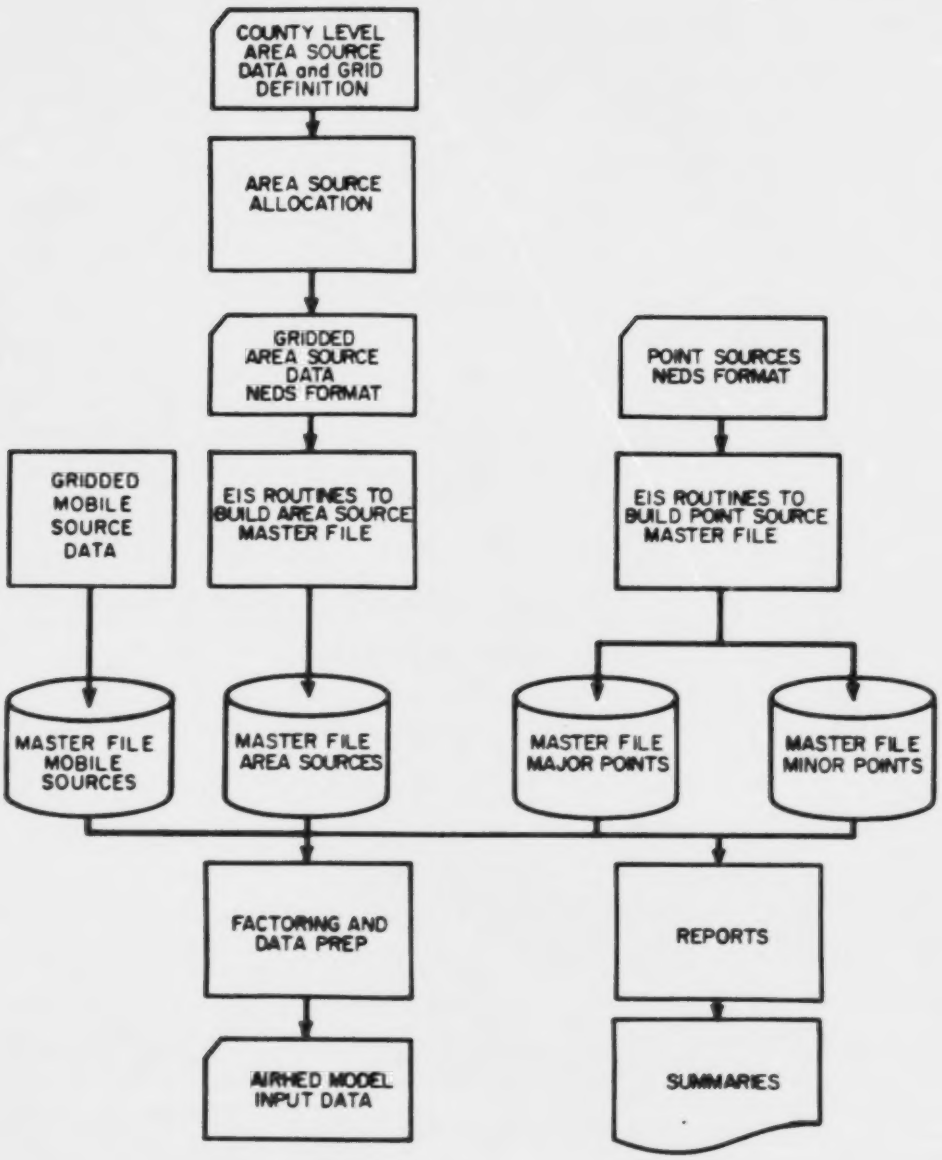



Figure 5: Flow Path of OMNYMAP Emissions Data

TABLE II

Summary of Emissions in Tons for Base (1980) and Scenario (1988)

| Scenario | New York | | New Jersey | | Connecticut | | Modeling Domain | |
|---|---|---|---|---|---|---|---|---|
| | VOC | $NO_x$ | VOC | $NO_x$ | VOC | $NO_x$ | VOC | $NO_x$ |
| BASE YEAR -1980 | 380,016 | 351,350 | 382,258 | 345,228 | 203,645 | 158,393 | 965,919 | 854,971 |
| Projection - 1988 | 241,193 | 292,149 | 272,802 | 324,339 | 140,291 | 122,369 | 654,286 | 738,857 |
| % Change from 1980 | -36.9 | -16.8 | -28.6 | -6.1 | -31.1 | -22.7 | -32.3 | -13.6 |
| Full SIP Implementation | 199,163 | 292,149 | 255,780 | 324,339 | 123,706 | 122,369 | 578,649 | 738,857 |
| % Change from 1980 | -47.6 | -16.8 | -33.1 | -6.1 | -39.3 | -22.7 | -40.1 | -13.6 |

and 21% and 19% from Connecticut; respectively, while for the projected year, they are 37% and 39% from New York, 42% and 44% from New Jersey and 21% and 17% from Connecticut.

## 2.2 UAM Simulation of the Ozone Concentration Field for Five Days and Model Performance Evaluation

Using the model inputs described earlier, the UAM was executed to provide hourly averaged ozone concentration fields for each of the five selected modeling days. In Figures 6 through 10 are shown the isopleths of predicted ozone concentrations for selected hours for each of the five days. One of the characteristic features associated with these simulations is the occurrence of a double peak over the modeling domain around the time of the occurrence of the ozone maximum; one peak over the northeastern portion of Connecticut and the other over the border areas of northeastern New Jersey and New York. Only in the case of JD80219(080680) was there no clearly defined double peak. Perhaps, a lower advection rate and limited vertical mixing could result in the merger of the two peaks into a single broad peak. Also in some instances, the peak over the New Jersey-New York region is higher than the one occurring over the Connecticut region suggesting the significance of the pollutant transport through the southern and western boundaries.

### 2.2.1 Paired Comparisons - All Data

It should be recognized that whereas the UAM predictions represent volume averaged hourly concentration values (averaged over the cell volume specified in the modeling domain), the measured concentrations are at monitoring stations represented by a point in space. Hence, model performance evaluation is not a trivial problem. In this study, model performance was evaluated by comparing measurements from

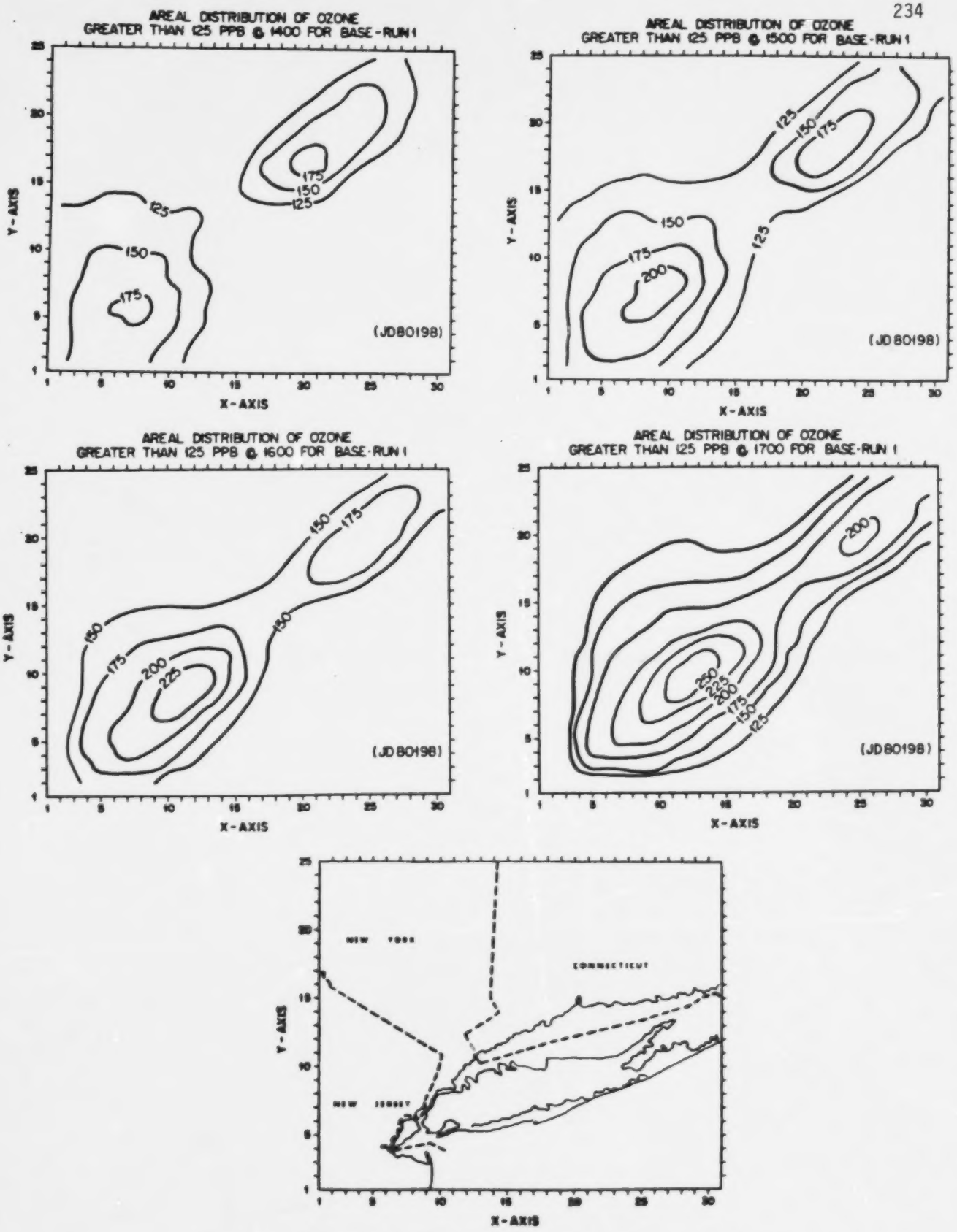



**Figure 6: Areal Distribution of Ozone Greater than 125PPb for JD80198 (071680) from 1400 to 1700**

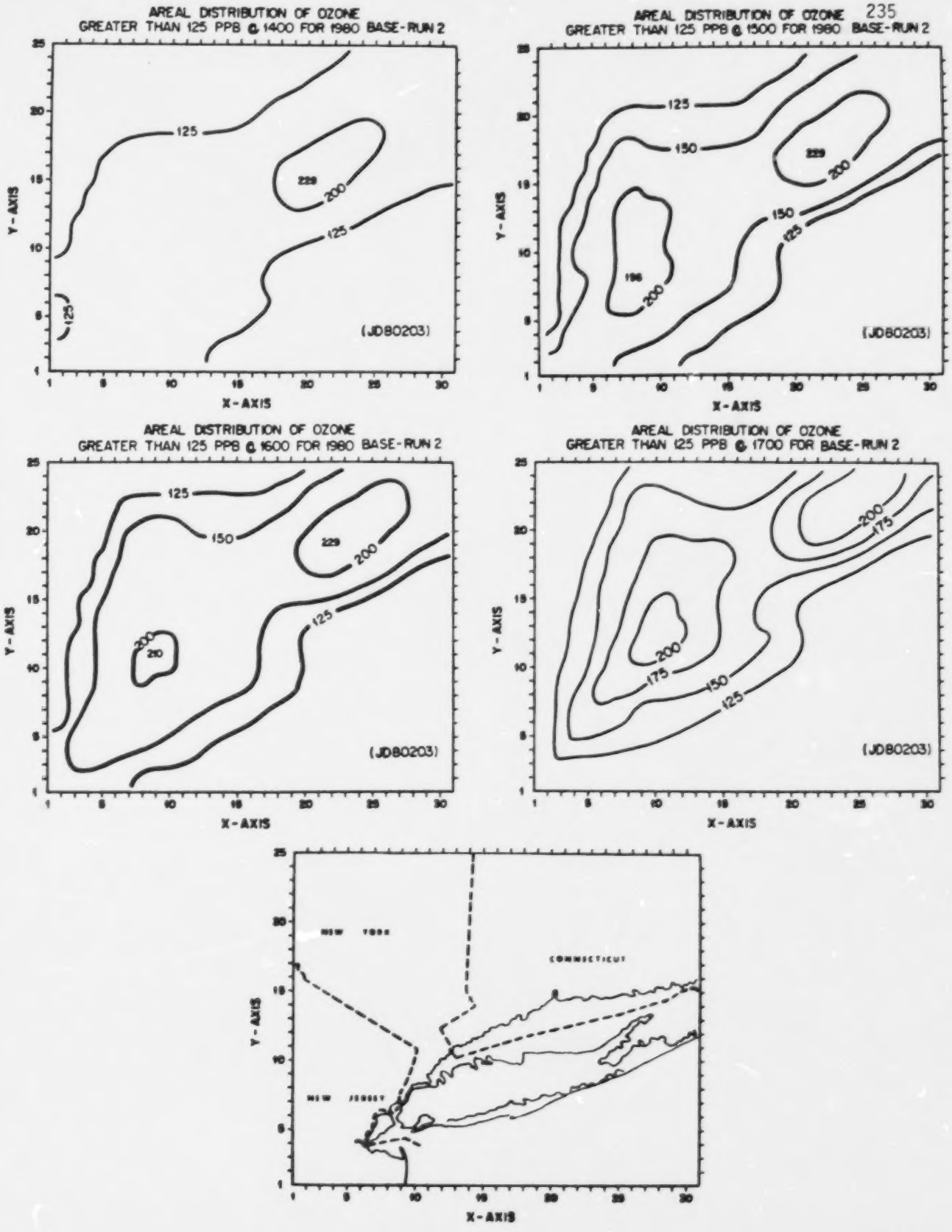



Figure 7: Areal Distribution of Ozone Greater than 125PPb for JD80203 (072180) from 1400 to 1700

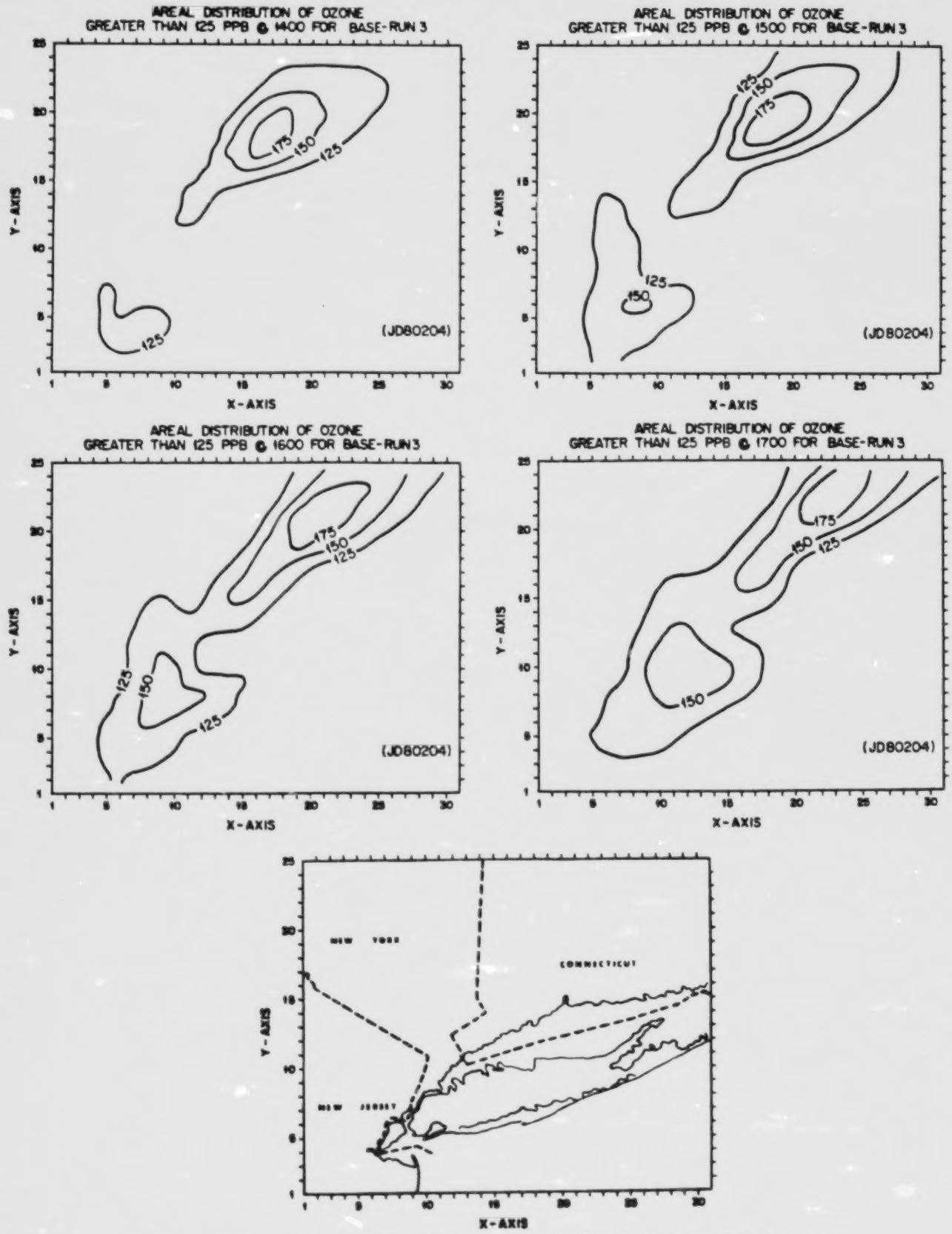



Figure 8: Areal Distribution of Ozone Greater than 125PPb for JD80204 (072280) from 1400 to 1700

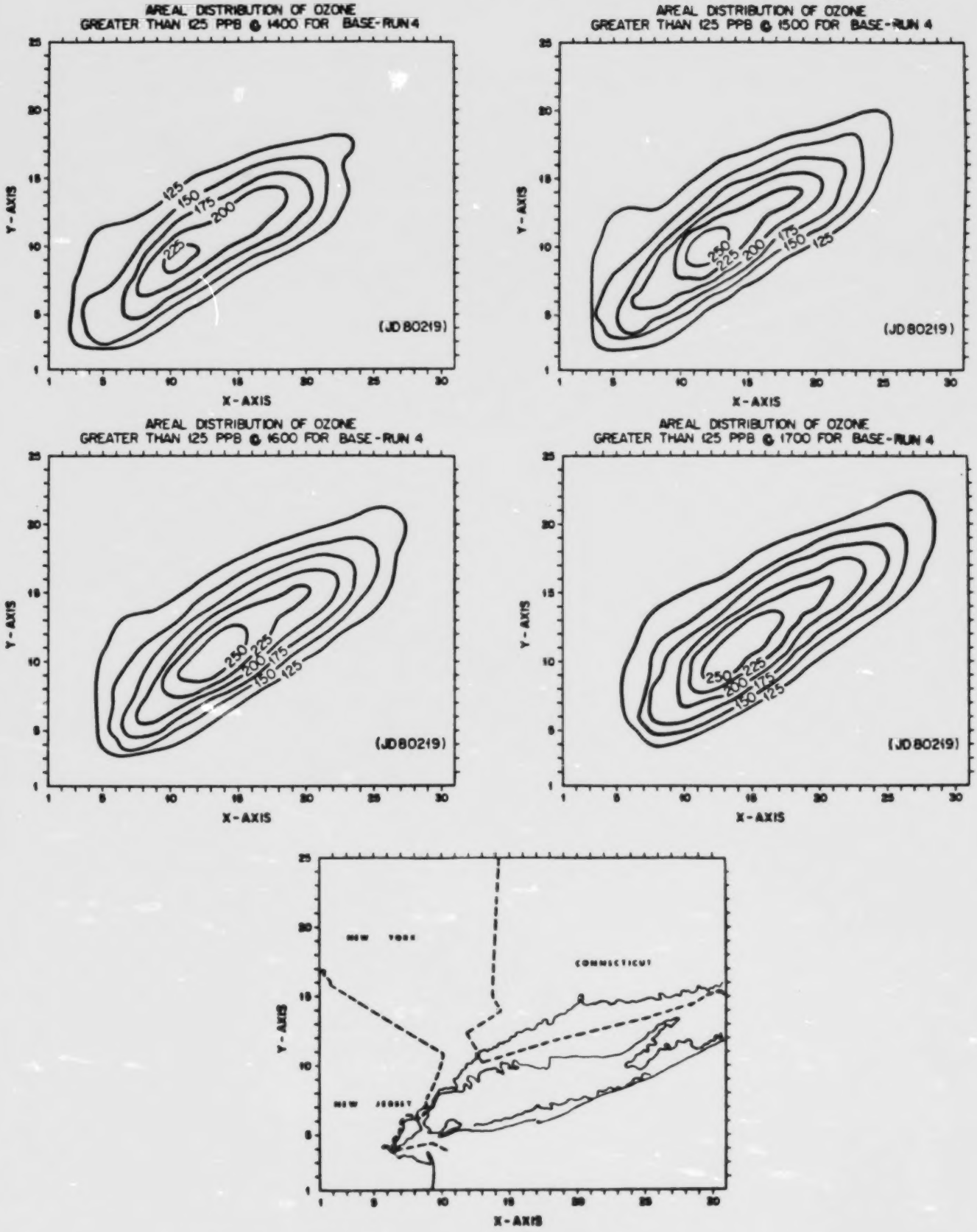



Figure 9: Areal Distribution of Ozone Greater than 125PPb for JD80219 (080680) from 1400 to 1700

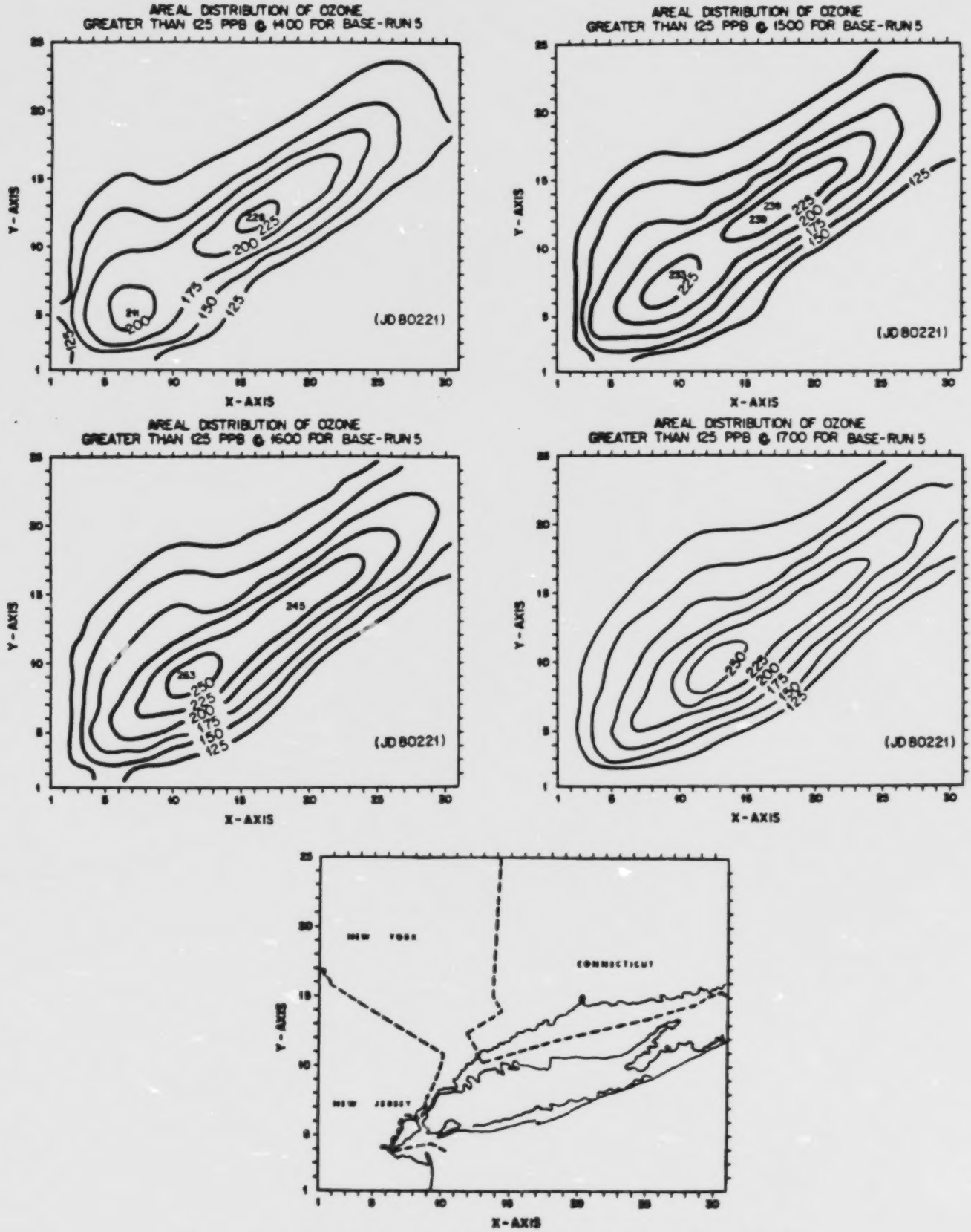



Figure 10: Areal Distribution of Ozone Greater than 125PPb for JD80221 (080880) from 1400 to 1700

monitoring sites to model predictions at the grid point nearest to each monitoring location. Figure 11 is a scatter plot of the observed and predicted concentrations for all data for each of the days considered in the study. In addition to the one-to-one line (perfect prediction), an envelope delineating ±30% of the observed concentrations is included in the figure by dashed lines; the percentage number of points lying within ±30%, greater than 30%, and less than 30% are provided in Table III. The percentage of predictions within the ±30% envelope for each of the days is around 30% or better, while the percentage of under-prediction is about 10%.

Several standard statistical measures (Willmott, 1981; Fox, 1981; Rao, et al., 1985) were computed for the predicted/observed data pairs and the results are summarized in Table IV. The high correlation coefficients ($r_{crit\ 0.95} \geq 0.098$) indicate that the model predictions are reasonable either when the data are considered on an individual day-byday basis or on an ensemble basis. However, on the average the model tends to overpredict the concentrations as indicated by the mean of the ratios predicted to the observed concentrations. Two days, JD80203(072180) and JD80221(080880), have the highest correlation coefficient and index of agreement.

### 2.2.2 Paired Comparison - Connecticut

The ozone measurements for the five days indicate that the peak concentrations occurred over Connecticut and therefore, it was decided to investigate the model performance in particular reference to this region. In Figure 12 is shown the scatter plot of observed versus predicted concentrations along with the ±30% envelope and in Table V are listed the percentage of points within, below and above the ±30%

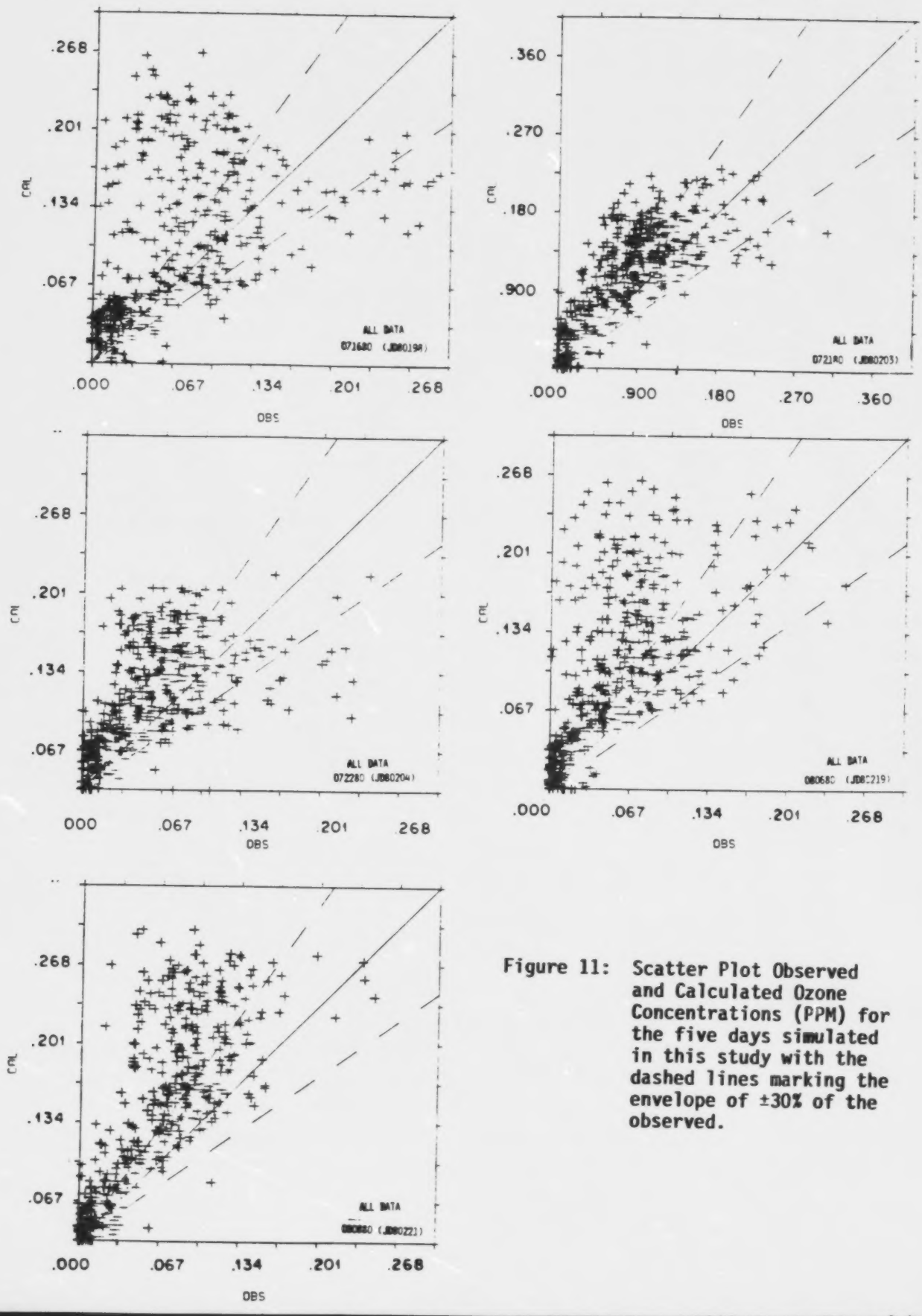



**Figure 11:** Scatter Plot Observed and Calculated Ozone Concentrations (PPM) for the five days simulated in this study with the dashed lines marking the envelope of ±30% of the observed.

TABLE III

Percentage of Over (>30%) and Under Prediction (<30%)
For All Ozone Data for the Five Selected Days

| | Day | | | | | |
|---|---|---|---|---|---|---|
| | JD80198 (071680) | JD80203 (072180) | JD80204 (072280) | JD80219 (080680) | JD80221 (080880) | All Data |
| Percentage Within ±30% | 34 | 46 | 35 | 29 | 33 | 36 |
| Percentage of Over Prediction | 53 | 44 | 53 | 63 | 60 | 54 |
| Percentage of Under Prediction | 13 | 10 | 12 | 8 | 7 | 10 |
| Sample Size | 418 | 432 | 422 | 422 | 408 | 2102 |

TABLE IV

Summary of Paired Comparison of Ozone Concentrations for All Data (ppm)

| | JD80198 (071680) | | JD80203 (072180) | | JD80204 (072280) | | JD80219 (080680) | | JD80221 (080880) | | ALL DATA | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | OBS | PRED | OBS | PRED | OBS | PRED | OBS | PRED | OBS | PRED | OBS | PRED |
| Range | .000 to .291 | .000 to .266 | .000 to .303 | .000 to .228 | .000 to .240 | .000 to .183 | .000 to .249 | .000 to .262 | .000 to .246 | .000 to .263 | .000 to .303 | .000 to .266 |
| Mean | .072 | .103 | .084 | .108 | .060 | .081 | .060 | .105 | .070 | .117 | .069 | .103 |
| Standard Deviation | .059 | .066 | .055 | .058 | .045 | .045 | .047 | .068 | .045 | .073 | .051 | .063 |
| Correlation Coefficient | .466 | | .760 | | .560 | | .571 | | .739 | | .600 | |
| Slope | .514 | | .794 | | .562 | | .827 | | 1.180 | | .744 | |
| Intercept | .066 | | .042 | | .048 | | .055 | | .035 | | .051 | |
| Mean of (P/O) | 2.413 | | 1.785 | | 2.070 | | 3.079 | | 2.057 | | 2.277 | |
| Std. Dev. of (P/O) | 3.129 | | 2.438 | | 3.122 | | 7.084 | | 2.392 | | 4.050 | |
| Mean Diff. (O -P ) | -.031 | | -.024 | | -.021 | | -.045 | | -.047 | | -.034 | |
| Std. Dev. of (O -P ) | .065 | | .039 | | .042 | | .056 | | .049 | | .052 | |
| Avg. Abs. Gross Error | .051 | | .036 | | .037 | | .052 | | .050 | | .045 | |
| Root Mean Square Error for the Difference (RMSE) | .072 | | .046 | | .047 | | .072 | | .068 | | .062 | |
| Index of Agreement | .638 | | .828 | | .698 | | .630 | | .692 | | .701 | |
| Mean Fractional Error (MFE) | -.107 | | -.078 | | -.084 | | -.146 | | -.138 | | -.111 | |
| MSEu | .003 | | .001 | | .001 | | .003 | | .002 | | .002 | |
| MSEs | .002 | | .001 | | .001 | | .002 | | .002 | | .001 | |
| MSEu/MSE (%) | 65 | | 66 | | 62 | | 60 | | 51 | | 66 | |
| MSEs/MSE (%) | 35 | | 34 | | 38 | | 40 | | 49 | | 34 | |
| Sample Size | 418 | | 432 | | 422 | | 422 | | 408 | | 2101 | |

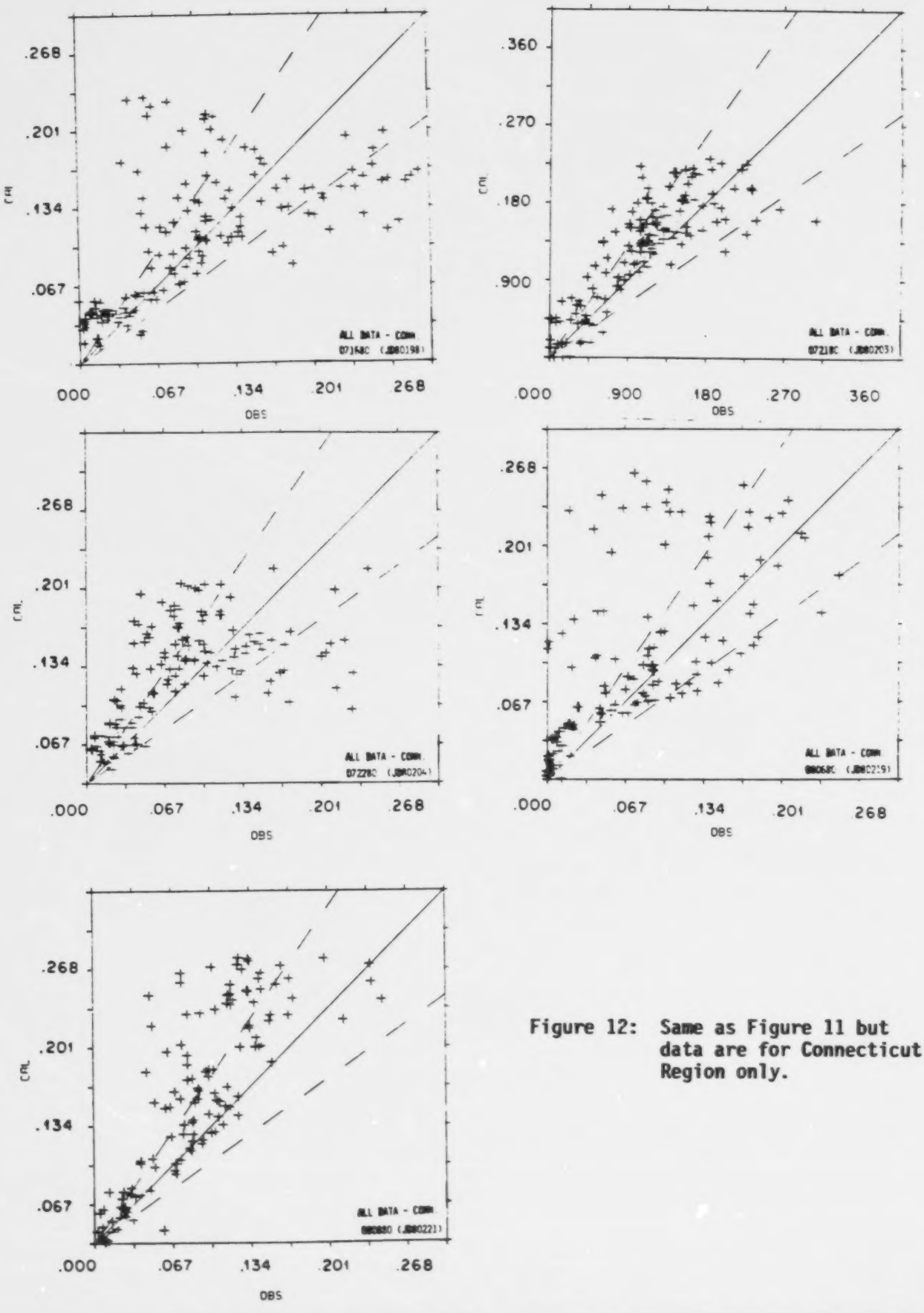



**Figure 12:** Same as Figure 11 but data are for Connecticut Region only.

TABLE V
Percentage of Over (>30%) and Under Prediction (<30%)
For All Ozone Data for the Five Selected Days
For the Connecticut Region

| | Day | | | | | |
|---|---|---|---|---|---|---|
| | JD80198 (071680) | JD80203 (072180) | JD80204 (072280) | JD80219 (080680) | JD80221 (080880) | All Data |
| Percentage Within ±30% | 49 | 64 | 46 | 43 | 50 | 51 |
| Percentage of Over Prediction | 35 | 27 | 42 | 48 | 44 | 39 |
| Percentage of Under Prediction | 16 | 9 | 12 | 9 | 6 | 10 |
| Sample Size | 142 | 140 | 139 | 127 | 125 | 673 |

envelope for each simulation day as well as for all Connecticut data from five days. The percentage of underprediction is about 10%, with about 50% of the data lying in the ±30% envelope. Of the five days simulated, the days JD80203(072180) and JD80221(080880) have 60% and 50% of the predictions within the ±30% envelope and only 6% and 9% of the data in the underprediction category, respectively. Examination of the ratios of predicted to measured concentrations for hours with measured values greater than 200 ppb indicates that the model often underpredicts with an average ratio of 0.73.

### 2.2.3 Paired Comparison - Concentrations Greater Than 100 ppb

It is important to analyze the model performance in terms of simulating high ozone concentrations so as to provide an assessment of the model's ability to capture the peak concentration values. To this end, only hourly measured concentrations greater than or equal to 100 ppb and their corresponding predicted values were examined as a set, for the domain as a whole, and Connecticut alone. The results, provided in Tables VIa and VIb respectively, indicate at least 60% of the data lie within the ±30% envelope in both cases with about 20% of the data on either side of the envelope. Also, on an individual basis, the two days JD80203(072180) and JD80221(080880) have the lowest percentage of data for the underprediction category with at least 60% or more of the data lying within the ±30% envelope.

### 2.2.4 Unpaired Comparison

The model performance can also be assessed through an unpaired comparison of the daily maxima of the measured and predicted concentrations at each of the monitoring stations independent of their time of occurrence. The ratio between the predicted and measured peaks ranges from 1.29 to 1.72 for the ozone monitoring network consisting of

TABLE VIa

Percentage of Over (>30%) and Under Prediction (<30%)

For Ozone Concentrations Greater than 100 ppb

For the Five Selected Days

| | Day | | | | | |
|---|---|---|---|---|---|---|
| | JD80198 (071680) | JD80203 (072180) | JD80204 (072280) | JD80219 (080680) | JD80221 (080880) | All Data |
| Percentage Within ±30% | 50 | 76 | 60 | 69 | 60 | 64 |
| Percentage of Over Prediction | 20 | 17 | 3 | 17 | 40 | 21 |
| Percentage of Under Prediction | 30 | 7 | 37 | 14 | - | 15 |
| Sample Size | 118 | 164 | 63 | 70 | 100 | 515 |

TABLE VIb

Percentage of Over (>30%) and Under Prediction (<30%)

For Ozone Concentrations Greater than 100 ppb

For the Five Selected Days

For the Connecticut Region

| | Day | | | | | |
|---|---|---|---|---|---|---|
| | JD80198 (071680) | JD80203 (072180) | JD80204 (072280) | JD80219 (080680) | JD80221 (080880) | All Data |
| Percentage Within ±30% | 59 | 80 | 65 | 56 | 60 | 66 |
| Percentage of Over Prediction | 10 | 14 | 4 | 21 | 40 | 17 |
| Percentage of Under Prediction | 31 | 6 | 31 | 23 | - | 17 |
| Sample Size | 68 | 84 | 46 | 43 | 52 | 293 |

28 stations over the tri-state region. The time difference or lag between the measured and predicted peaks ranges from ±2 Hrs for the New Jersey stations to ±5 Hrs for locations in Connecticut with the New York sites falling in between. However, it should be recognized that, in general, location of the model predicted ozone maximum may not necessarily be associated with those locations where ambient air quality measurements are available. Thus, in Table VII are listed for comparison the maximum measured and predicted ozone concentrations (independent of time and space) for all the five days. It should be noted that the measured ozone maxima for these five days are reported from the monitoring stations in Connecticut, as are the predicted values. The ratio of predicted to measured hourly maximum concentrations are in the range of 0.70 to 1.00 within a time lag of 0 to 3 Hrs. This suggests that the model underpredicts the peak value over the modeling domain as well as lags in terms of the time of occurrence of the maximum. The difference may be due to numerous factors such as the uncertainty in the specification of the initial and boundary pollutant concentrations, space and time variation in the adopted mixing height, and the wind fields as well as the lack of day to day variations in the emissions data.

Summarizing the results of the above analysis, it should be evident that the UAM performance in this application is comparable to its performance at other urban areas such as Tulsa (Reynolds, et al., 1982), St. Louis (Cole, et al., 1983) and Philadelphia (Haney and Braverman, 1985). Even though the model underpredicts the peak or maximum concentration over the modeling domain, it was found that at least 64% of the data are within the ±30% envelope for measured concentrations greater than 100 ppb. The paired and unpaired comparisons as well as the model's ability to predict peak or maximum concentrations over Connecticut reveal that the UAM simulations for the days JD80203(072180) and JD80221(080880) show better model performance than the other three days.

TABLE VII

Base Case Simulations for OMNYMAP Unpaired Spatially and Temporally

| | Concentration (PPb) | | | | |
|---|---|---|---|---|---|
| | Measured+ | | Predicted++ | | |
| Day | Max | Hr | Max | Hr | Ratio |
| JD80198(071680) | 291 | 14-15 | 205 | 17-18 | 0.70 |
| JD80203(072180) | 303 | 15-16 | 229 | 15-16 | 0.76 |
| JD80204(072280) | 240 | 16-17 | 191 | 16-17 | 0.79 |
| JD80219(080680) | 249 | 13-14 | 229* | 15-16 | 0.92 |
| JD80221(080880) | 246 | 13-14 | 246 | 16-17 | 1.00 |

+Measured at any monitor in the Connecticut Region
++Predicted at any grid in the Connecticut Region
*Peak in Connecticut Merged into the Secondary Peak

## 3. Future Year Simulations

The major thrust of this study was to evaluate the effectiveness of control strategies of precursor emissions for attainment of the ozone NAAQS in the New York Metropolitan area. The two days with "best" model performance JD80203(072180), JD80221(080880) were selected for further examination of the impact of the emission reduction plans on the ambient ozone concentrations. An emissions inventory for 1988 based upon the 1982 SIP was prepared and the UAM simulations were performed for these two days with appropriate modifications, as described below, to the initial and boundary air quality conditions. In this section, the results of these control options are presented and compared with the base case to examine the effect of various emission reduction plans on the ambient ozone concentrations in the study region.

### 3.1 Initial and Boundary Conditions

For estimating 1988 initial conditions, a comparison was made between the 1988 $NO_x$ and VOC emissions and those of the 1980 base case and the percentage reductions for these two pollutants were calculated. The base year initial VOC and $NO_x$ concentration fields as well as those for the layers up to the base of the vertical layer 4 were then scaled by these estimated percentage reductions at the surface level. The 1988 boundary concentrations of VOC and $NO_x$ were obtained on the basis of the proposed upwind SIP's by reducing the base year concentrations by 40% and 20%, respectively. In the case of ozone, no direct methods are available to estimate the future year boundary and initial fields due to the changes in the precursor emissions levels. Given that the ozone concentrations at the top of the modeling region for the five simulated days in the base year are in the range of 60 to 85 ppb, the proposed changes in the emissions both upwind and in the domain could result in a reduction of about 20 to 30% or in the 40 to 60 ppb range for ozone levels at the top of the modeling domain. These estimates are consistent with the suggested

background levels (Wolff and Lioy, 1978; Kelly, et.al, 1984). Another method is to apply the EKMA procedure (EPA, 1984) to estimate the expected changes in the ozone concentrations from changes in the VOC and $NO_x$ levels. This procedure, results in a reduction of about 18% in ozone for an assumed change in the VOC and $NO_x$ levels of 40% and 20%, respectively. In this analysis, as a first approximation, the initial and boundary fields and region top ozone levels of the 1980 base year were reduced by 20% for the future year simulations.

## 3.2 Control Strategies

The control strategies imposed on the emissions data were based on the formulation developed in the SIPs for 1982 by each of the three States involved. Results from two emission control strategy simulation scenarios (CSSS) are presented here. The CSSS runs 1 and 2 are based on the projected 1988 emissions with meteorological conditions prevailing on JD80203(072180) and JD80221(080880), respectively. The overall reduction in VOC and $NO_x$ emissions from the 1980 base year are 32% and 14%, respectively (see Table 2). The CSSS run 3 included the adoption of several extraordinary measures which yield an additional 8% reduction in VOC emissions over the CSSS run 1 case in the tri-state area, with the meteorological conditions prevailing on JD80203(072180).

## 3.3 Results and Discussion

The areal distributions of ozone for CSSS runs 1 and 2 for the peak ozone hours are shown in Figure 13. For both days, the distribution shows the occurrence of a double peak similar to the base case although the peak value over Connecticut has decreased from 229 ppb to 185 ppb for the 0721 case, and from 245 ppb to 200 ppb for the 0808 case. The relative reduction in the peak ozone concentration is approximately 19% in both cases for an emissions reduction of 32% in the VOC's and 14% in the $NO_x$ over the modeling domain. The areal

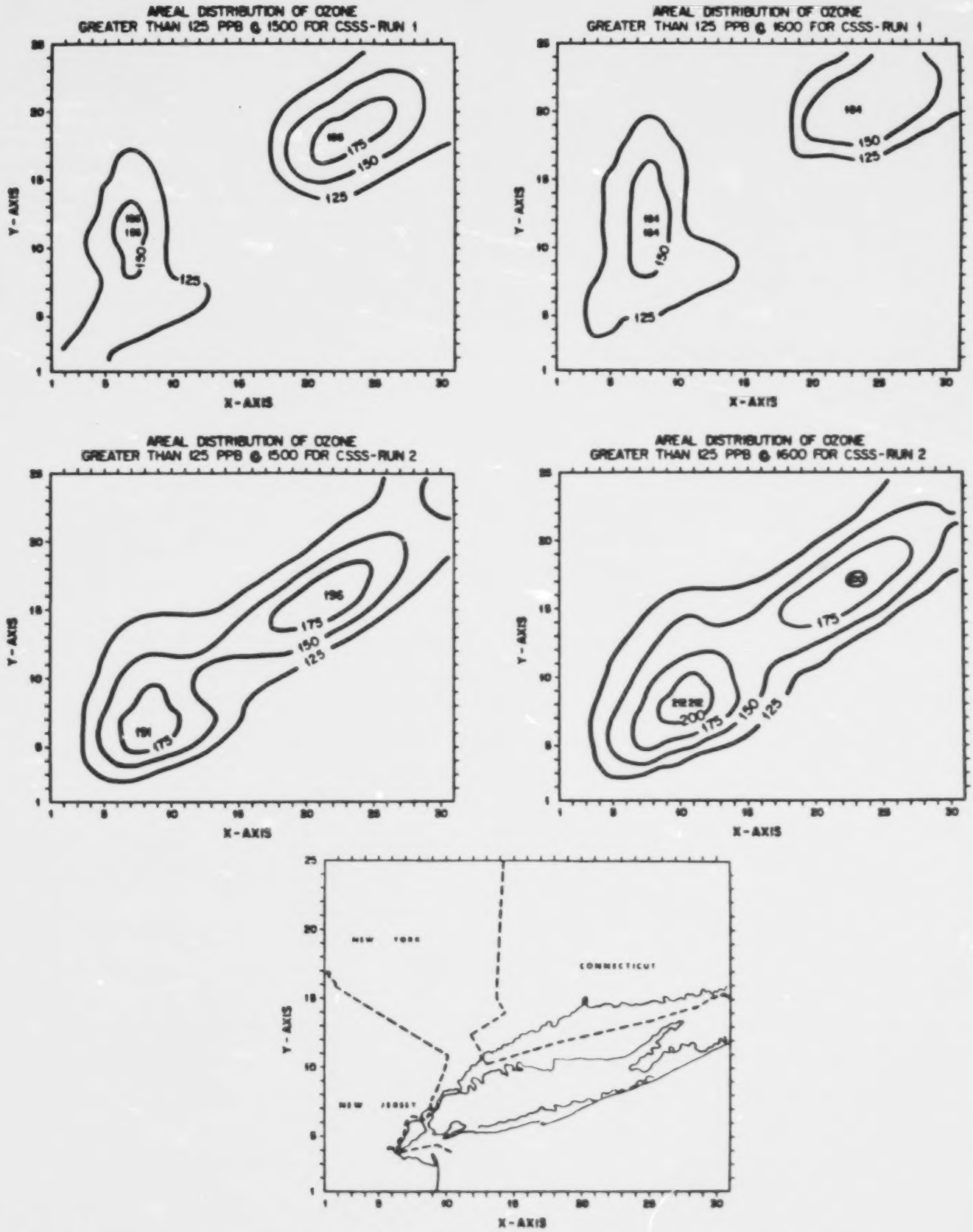



Figure 13: Areal Distribution of Ozone Greater than 125PPB for Selected Hours With 1988 Emissions and Meteorological Data from July 20 and August 8, 1980

extent of the decrease in ozone concentrations above the level of the NAAQS was obtained by calculating the number of grid cells at or exceeding the threshold concentration of 125 ppb for each hour starting at 0900 hr. This is shown as a histogram plot in Figures 14a and 14c for the entire modeling domain (667 cells) and for the Connecticut region (208 cells) in Figures 14b and 14d. On a percentage basis, the decrease in the number of cells (areal extent) for the peak ozone hour of 1500 is about 50% for 0721 compared with about 20% for the 0808 case for the entire domain as well as for the Connecticut region. This may be due to the differences in the prevailing meteorological conditions on these two days.

CSSS run 3 includes control strategies requiring further reduction in the 1988 emissions with the imposition of controls on gasoline vapors in New York and Connecticut (refueling of motor vehicles) and the implementation of controls on (a)architecture coatings, (b)auto refinishing, (c)consumer/commercial solvents, and (d) small source RACT in the tri-state region. In Figure 15 are shown the ozone isopleths for the CSSS run 3. The peak predicted ozone concentration is 175 ppb compared with 185 ppb for the case of CSSS run 1. The areal extent or the number of cells exceeding 125 ppb for the CSSS run 3 is shown in Figures 14a and 14b for the entire domain and for Connecticut only. Comparisons between the results of CSSS run 1 and CSSS run 3 reveal that the percentage changes in the areal extent are in the range of 8 to 10% for the entire domain, as well as for Connecticut alone. It is evident that while the reduction in emissions under the CSSS run 3 has resulted in a further reduction in the areal extent of the ozone exceedances, these emissions reductions have not resulted in ozone levels at or below the ozone NAAQS.

## 4. Summary and Conclusions

In this study, the UAM was used to simulate five high ozone days of the 1980 oxidant season. These five high ozone days were

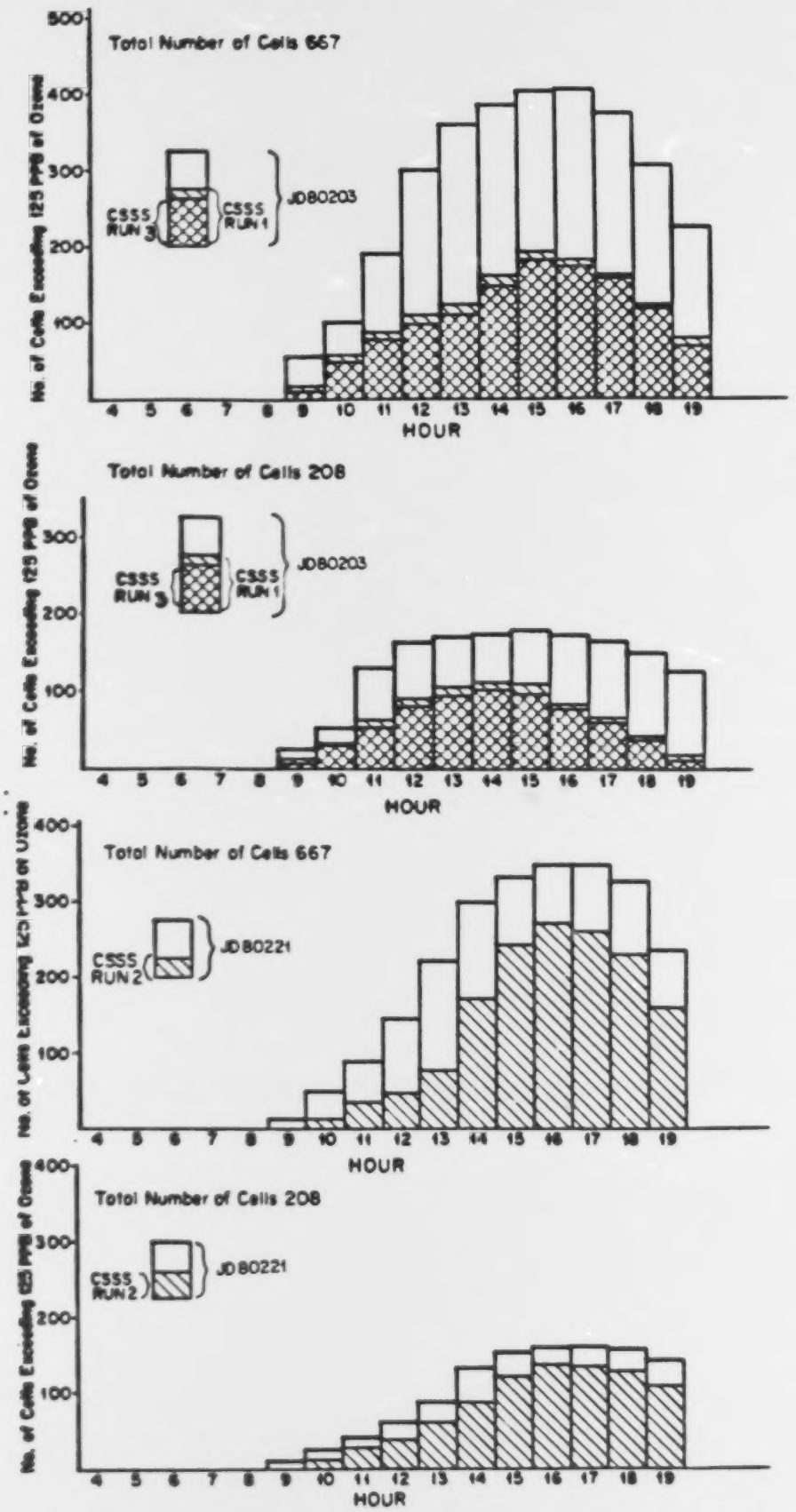
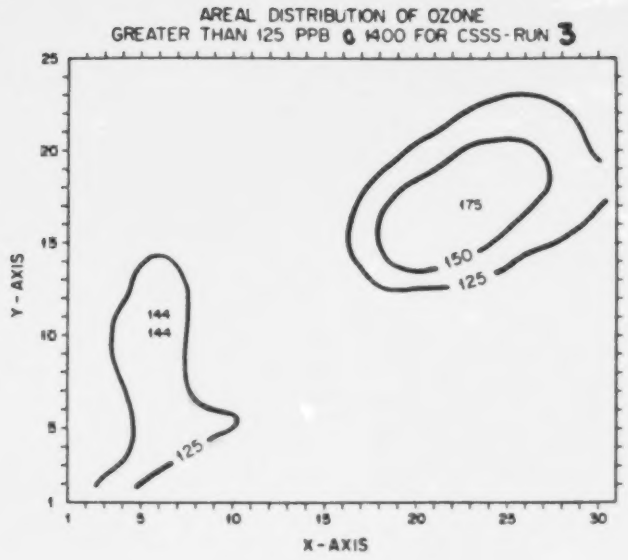
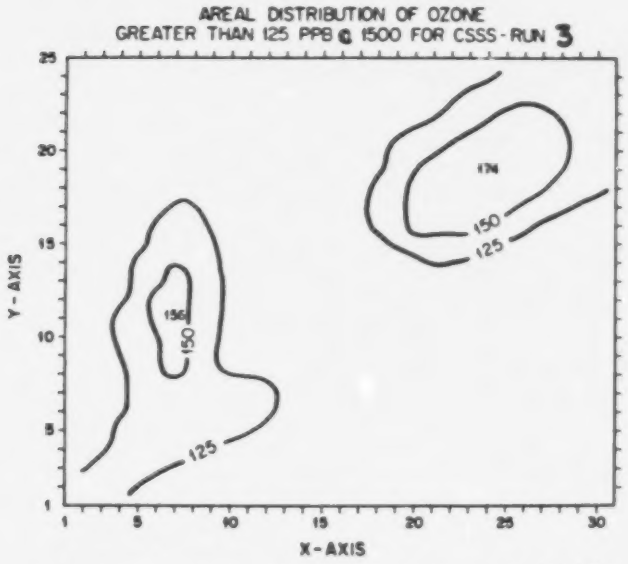



Figure 14: Histogram Plot of Number of Cells Exceeding Ozone Concentration of 125PPb for the BASE and Scenario Runs



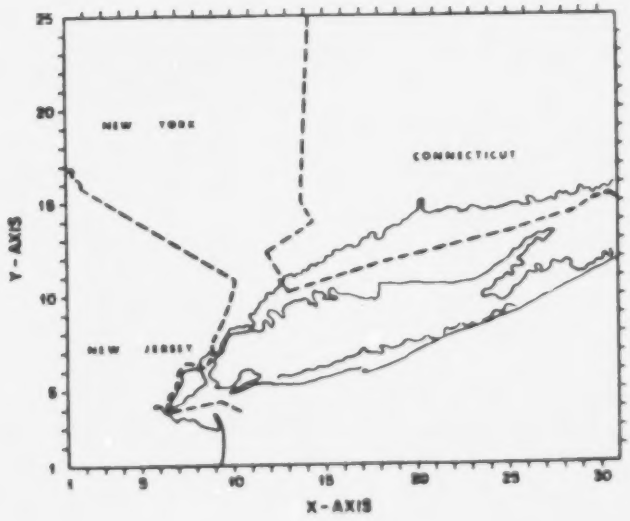




Figure 15: Areal Distribution of Ozone Greater than 125PPb for 1988 Emissions with Extraordinary measures and 072180 meteorology

characterized by exceedances of the NAAQS over wide areas of the New York Metropolitan area consisting of portions of the States of New Jersey, New York and Connecticut. The meteorological features associated with these days are (a) winds from south to southwest at about 4 to 5 m/s, (b) maximum surface temperatures in the mid to upper 90°F, and (c) a high pressure system over the Atlantic and westward through the southern states.

The New York Metropolitan area covers a portion of the emissions-rich northeast urban corridor with considerable inter-urban transport of pollutants from upwind areas. Four of the five days simulated show the occurrence of two peaks with a peak occurring over central Connecticut attributable primarily to the emissions from the NY/NJ area and another peak occurring over Northeastern New Jersey and New York border areas as a result of transport from upwind regions through the lateral boundaries.

The first part of the study was designed to apply UAM to the New York Metropolitan area and assess the model performance in terms of its ability to simulate the observed ozone concentration field. To this end, it was determined that even though the model has a tendency to underestimate the peak ozone concentration over the modeling domain, the performance of the model to predict within ±30% envelope of the measured levels is reasonable both on an individual day basis as well as on an ensemble basis. The performance statistics for concentrations greater than 100 ppb over the Connecticut region revealed that 60% of the model predictions lie within the ±30% of the observed concentration envelope. Of the five days that were simulated, two days, JD80203(072180) and JD80221(080880), were selected for detailed evaluation of the State Implementation Plans adopted by the three states. The reductions in the VOC and $NO_x$ emissions in the New York Metropolitan area in 1988 are estimated to be 32% and 14% respectively from the 1980 base line and approach 40% for VOC when additional controls are imposed upon such source categories as architectural

coatings, auto refinishing, consumer/commercial solvents and adoption of small source RACT. It was also assumed that there will be concurrent reductions in the upwind emissions regions which would reduce the boundary concentration levels by about 40% for VOC, 20% for $NO_x$, and 20% for ozone.

The results of the UAM simulation with projected 1988 emissions for the two selected days indicate that the peak ozone concentration over the Connecticut region decreased by about 20% from the base year but still is well above the level of the ozone NAAQS. The areal extent of the decrease in exceedances of the NAAQS ranged from about 20 to 50% depending upon the simulation day. Clearly, additional modeling analyses should be performed to determine the level of control needed to meet and maintain the ozone NAAQS in the New York Metropolitan area.

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# A THEORETICAL STUDY OF REGIONAL OXIDANT DISTRIBUTION IN NORTH AMERICA

(Text not provided)

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# OXIDANT FORMATION AND TRANSPORT FROM PETROCHEMICAL COMPLEX EMISSIONS IN ONTARIO

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## RÉSUMÉ

Durant la période du 27 juin au 18 juillet 1984, une étude sur le terrain a été menée de façon intensive dans la région de Sarnia en Ontario. Les principaux objectifs de cette étude étaient:

1. de déterminer les taux d'ozone dans le sud-ouest de l'Ontario dus aux émissions d'hydrocarbures et d'oxydes d'azote ($NO_x$) provenant de Sarnia;

2. d'évaluer les conditions météorologiques pour lesquelles les contributions de Sarnia forment une part importante des niveaux totaux d'ozone dans le sud-ouest de l'Ontario.

Aux données provenant du réseau de surveillance sur la météorologie et la qualité de l'air, on a ajouté des mesures additionnelles prises durant la période d'étude. De plus, un avion équipé d'instruments a été utilisé pour produire une carte de l'ozone et des autres espèces de cette région.

Les principales conclusions qui ressortent de l'étude sont les suivantes:

1. Les émissions de précurseurs d'oxydants de la région de Sarnia peuvent mener à la formation de forts taux d'ozone sous le vent. Selon les résultats obtenus durant la période d'étude, on peut s'attendre à des répercussions mesurables environ 30 pour cent du temps durant les jours ensoleillés d'été, surtout lorsque les vents sont faibles et quand le brassage atmosphérique est nul.

2. Dans de telles occasions, on peut aussi s'attendre à un accroissement maximum de l'ozone (au-dessus des niveaux régionaux de fond) jsuqu'à 20-40 parties par milliard (ppb). Les régions touchées peuvent atteindre de 100 à 1000 $km^2$ et les répercussions peuvent durer plusieurs heures. De temps à autre, les contributions de Sarnia aux teneurs totales en oxydants provoquent une hausse des concentrations horaires d'ozone au-dessus du maximum provincial permis de 80 ppb.

3. D'après la fréquence des accroissements d'ozone attribuables aux émissions de Sarnia, la dimension du territoire touché (environ un pour cent du territoire du sud de l'Ontario où l'ozone excède fréquemment les critères provinciaux de la qualité de l'air) et l'ampleur des contributions de Sarnia en comparaison avec les valeurs régionales de fond, il est évident que les concentrations d'ozone du sud-ouest de l'Ontario en été dépendent fortement des émissions importées plutôt que des émissions locales.

4. À l'heure actuelle, il est difficile de savoir si la formation des oxydants dans la région est limitée par les $NO_x$ ou les hydrocarbures.

**Abstract**

During the period June 27 - July 18, 1984, an intensive field study was carried out in the Sarnia area of Ontario, with the following primary objectives:

(i) to determine the contribution to ozone levels in southwestern Ontario caused by hydrocarbon and nitrogen oxide precursor emissions at Sarnia; and

(ii) to determine the meteorological conditions under which the Sarnia contribution makes up an important portion of the total ozone levels in southwestern Ontario.

The regular air quality and meteorology monitoring network was supplemented with additional measurements for the study period, and an instrumented aircraft was used to assist in the mapping of ozone and other important species in the study area.

The main conclusions of this study are:

(i) Oxidant precursor emissions from the Sarnia area can lead to the formation of elevated ozone levels downwind. On the basis of the results obtained during the study period, a measurable Sarnia impact would be expected to occur about 30% of the time during the summer months, on sunny days, especially with low wind speeds and inhibited atmospheric mixing.

(ii) On these occasions, maximum ozone buildups (above regional background levels) up to about 20-40 ppb can be expected. The affected areas can be on the order of 100-1000 $km^2$ in size, and the duration of the impact, several hours. At times, the Sarnia contribution to the total oxidant levels can push hourly ozone concentrations over the provincial air quality criterion of 80 ppb.

(iii) Nevertheless, judging from the frequency of occurrence of ozone buildups attributable to Sarnia emissions, the size of the area affected (on the order of 1% of the total area of southern Ontario, where exceedences of the provincial air quality criterion of ozone are frequently observed), and the magnitude of the Sarnia contribution compared to regional background values, it is clear that ozone levels in southwestern Ontario in the summer are largely governed by the imported component, rather than ozone generation from local emissions.

(iv) It is not clear at present whether oxidant formation in the area is $NO_x$- or hydrocarbon-limited.

## Introduction

Ontario's air quality criterion for ozone (0.08 ppm hourly average) is frequently exceeded during the growing season (June, July and August) in southwestern Ontario. It has been estimated that, if control efforts could succeed in meeting the above criterion in all sections of the province, farmers would benefit by more than $20 million a year in extra production of various agricultural crops, such as tobacco, soybeans, wheat and white beans (Linzon et al., 1984).

A number of studies have examined the meteorological conditions accompanying ozone episodes in southern Ontario (Mukammal, 1965; Yap and Chung, 1977; Chung, 1977; Anlauff et al., 1977; Shenfeld et al., 1978; Mukammal et al., 1982; Heidorn and Yap, 1984). It has been found that elevated ozone levels commonly occur over widespread areas during the spring and summer, typically on the rear sides of anti-cyclones or in the warm sectors of cyclones. While long-range transport from the northeastern United States is strongly implicated as the cause of ozone concentrations during these conditions, there is also evidence of ozone formation from local emissions in southern Ontario. For example, Shenfeld et al., (1978) have found ozone "bulges" around the Metropolitan Toronto and Windsor - Sarnia areas during episode days in 1978, which are most probably due to locally emitted ozone precursors.

The existence of such "bulges" around significant hydrocarbon and nitrogen oxide source areas is to be expected, in view of a number of field studies which have shown buildups of ozone a few hours downwind of urban and industrial areas of various types (see, for example, Westberg et al., 1981; van Duuren et al., 1981; Neuber et al., 1981; Spiecer et al., 1982; Sexton, 1983; Sexton and Westberg, 1983a and 1983b). The Sarnia area, with its concentration of petrochemical industries, was thus of considerable interest, because of both its location in a portion of Ontario which is already subject to heavy ozone loadings due to long-range transport from the south, and its role as an important emitter of hydrocarbons and nitrogen oxides. Table 1, for example, shows the emission density of nitrogen oxides

and several classes of hydrocarbons in the Sarnia area. The nitrogen oxide emissions are contributed approximately equally by area sources (primarily vehicular traffic in Sarnia) and a large thermal power generating station on the St. Clair River, about 20 km south of Lake Huron. The hydrocarbon emissions are distributed among a number of refineries and petrochemical plants near the St. Clair River, and within about 20 km of Lake Huron.

Accordingly the Sarnia Oxidants Study was carried out by the Air Resources Branch of the Ontario Ministry of the Environment (MOE). The Lambton Industrial Society and York University also participated. The study was part of Ontario's Oxidant Control Strategy Development, and had the following objectives:

(i) to determine how much ozone, over and above "background" levels imported into the area, is contributed by precursor emissions from Sarnia itself;

(ii) to determine under what meteorological conditions Sarnia contributions make up an important portion of the total ozone levels in southwestern Ontario, as compared to long-range transport; and

(iii) to determine which precursor ($NO_x$ or hydrocarbons) should be controlled in order to lower oxidant levels in the Sarnia area.

During the period June 27 - July 18, 1984, extensive measurements were made of ozone precursors, using supplementary ground-based monitors (in addition to the regular air monitoring network) and an instrumented aircraft. The existing meteorological network was also enhanced with acoustic sounder and minisonde measurements. The details on monitoring techniques and observations from these individual measurement programs are reported in a number of Ontario Ministry of Environment reports (see Ministry of the Environment, 1985), as well as by Hastie and Schiff (1984). This paper briefly discusses some of the main results from the study. A detailed analysis of the air quality and meteorological data has been reported by Lusis et al. (1985).

**The Measurement Program**

During the Sarnia Oxidants Study, an extensive data set was collected both on the ground and aloft. In addition to the pollutants monitored routinely ($O_3$, NO and $NO_x$, $SO_2$, CO, hydrocarbons) at a number of Ministry of the Environment Stations in the study area, several specialized air quality measurements were made. These included:

(i) Hydrocarbon speciation of samples collected (as hourly averages by) MOE mobile laboratories at Courtright and Camlachie, as well as on the aircraft (as 15 or 30 minute averages) during flights upwind and downwind of Sarnia.

(ii) Measurements of aldehydes, ketones, acetates and alcohols: formaldehyde was monitored at Camlachie by the York University group using their tunable diode laser spectrometer (TDLAS). The other compounds were monitored at Courtright, using MOE's trace atmospheric gas analyser (TAGA), a quadrupole mass spectrometer with an atmospheric pressure chemical ionization front end.

(iii) Measurements of some other parameters indicative of photochemical activity in the air mass: these included hydrogen peroxide (by TDLAS at Camlachie); and light-scattering particulates, sulfates and nitric acid (by nephelometer and filter pack in the aircraft).

(iv) High-sensitivity measurements of NO and $NO_x$ at Camlachie, using a modified chemiluminescent analyzer developed by York University.

(v) Ozone precursor measurements: the ozone precursor monitor has been described by Belanger and Ortman (1984). Two such instruments were deployed, at Courtright and Camlachie, where concurrent measurements were being carried out on nitrogen oxides and hydrocarbons. Basically, the ozone precursor monitors are reaction chambers where ozone content is measured before and after artificial irradiation

(with u.v. lamps) of an ambient air sample. It was hoped that an analysis of the ozone levels before and after irradiation, together with the concurrent $NO_x$ and hydrocarbon monitoring results, would give information on which precursor species contributes most to ozone levels in the Sarnia area.

The meteorological measurements collected by the regular towers were also supplemented, notably by an acoustic sounder to measure atmospheric stability (at Petrolia) and by two minisonde stations (at Petrolia and Camlachie) to measure wind speed and temperature as a function of height.

Figure 1 shows the location of monitoring sites which provided data for this study. The air quality and meteorological measurements made at each location (as well as the aircraft) are summarized in Table 2.

For details of the monitoring techniques used, the reader is referred to a series of Ministry of the Environment reports listed in the References section (Ministry of the Environment, 1985).

It should be noted that at the beginning and toward the end of the study period, all $O_3$, $NO_x$ and hydrocarbon analyzers in the Sarnia area which were involved in the study were audited by the Ministry's Instrumentation Unit, thus ensuring comparability of the results.

The Sarnia Oxidants Study was designed to take maximum advantage of the air quality mapping capabilities of the aircraft. A tradeoff had to be made between spatial coverage and vertical resolution, since only one aircraft was available, with an endurance of about 5 hours. We chose the former. Since the principal objective of this study was to identify the effect of the Sarnia petrochemical complex on ozone levels in southwestern Ontario, most of the aircraft sampling consisted of crosswind transects, within the mixing layer at various distances downwind of Sarnia. However, upwind transects were also carried out, to establish the background levels. On some occasions spirals were flown, to determine the vertical pollutant structure. There were

also some other deviations from this procedure. For example, on July 8, when winds were light and variable, samples were collected over the Sarnia area itself, in order to get a measure of ozone, hydrocarbon and nitrogen oxide concentrations in air parcels freshly exposed to Sarnia emissions.

A total of fourteen flights, each lasting typically for two to four hours, were carried out during the study period. During the flight days, minisondes were released (every hour or every two hours, depending on the meteorological conditions on the day in question) and hydrocarbon samples were collected for speciation by gas chromatography. Radio contact was maintained between the base station at Sarnia airport, the mobile units at Courtright and Camlachie, the minisonde crew at Petrolia, and the aircraft, so that information updates on meteorological and ground-level air quality conditions could be relayed to the aircraft. In this way it was possible to alter if necessary the flight plans which had been formulated in the morning, in consultation with the Sarnia airport weather office, and thus optimize the usefulness of the collected data.

**Discussion of Results**

Space limitations preclude a detailed discussion of the results, which may be found in the report by Lusis et al. (1985). However, we include below a fairly typical example of the type of data obtained, based on one of the study days - July 14. Figure 2 shows the variation of ozone at the surface monitoring sites in the study area, while Figures 3(a)-(d) include both aircraft and ground-level measurements during successive hours when flights were carried out. Near each surface monitoring site is shown the average ozone concentration in ppb during the hour (urban data are not shown because of scavenging by local nitric oxide emissions). The location of the particular aircraft traverse(s) flown during the hour is shown as a broken line, with the traverse number shown at the starting point. The trace around each aircraft traverse represents (instantaneous) ozone concentrations, with minimum and maximum measured values (in brackets) shown at the appropriate locations, and the overall average for the traverse (also in brackets) shown

at the end of the traverse. Figures 3 (a)-(d) also include the time when each traverse started and ended, and the wind speed and direction at the approximate aircraft sampling height, as determined from the minisonde measurement made at the Petrolia site.

On July 14, a quasi-stationary high pressure system was centered in the vicinity of Kentucky, West Virginia. To the north, a quasi-stationary frontal system extended in an east-west line through the upper Great Lakes. The Sarnia region was in a post-ridge/pre-warm front situation, and experienced gradient winds with a southerly component. During the period 0900-1200 EDT, when the aircraft flights were conducted, winds were from the west-southwest, with speeds in the 10-20 km $h^{-1}$ range. Scattered clouds occurred, with temperatures in the mid-to upper twenties. The maximum total solar radiation (0.3 - 3 micron range) rose to slightly in excess of 80 milliwatts $cm^{-2}$ (by noon); the surface relative humidity was in the 50-60% range for most of the flight period. The minisonde data suggest an initial mixed layer of 150 m, gradually increasing to about 1000 m by noon. In the early morning, until 0800 hours, a brown haze was visible over the Sarnia area, with portions advected over Lake Huron, and other portions going off in an easterly direction.

During the study period, forward trajectories from Sarnia show a northeastward movement. On the other hand, backward trajectories (48 hours) of air parcels over the Sarnia area indicate slow movement from Illinois northeastwards.

Because of the southerly origins of the air entering the study area on this day, a relatively high upwind loading of pollutants was observed. Aircraft nephelometer measurements upwind of Sarnia showed that the light-scattering coefficient was about $1 \times 10^{-4} m^{-1}$ with occasional higher values due to broad plumes, while the high volume sampler gave sulfate and nitrate levels of 54 and 20 ug $m^{-3}$ (however, these levels may be so high because portions of the Detroit/Windsor plume may have been sampled during part of the upwind traverse). During the time of the flight, ozone levels increased rapidly across the network (Figure 2), and by late afternoon had exceeded the provincial hourly air quality criterion of 80 ppb at most stations.

The rapid change in meteorological conditions in the period immediately before, and during the first hour or so, of the study (i.e. rapid growth of the mixing layer, winds changing from southerly to west-southwesterly), makes the data interpretation somewhat difficult. With the exception of a spiral carried out at the end of the flight, an altitude of about 200 m above ground level was maintained by the aircraft. Since the sampling aloft was started soon after 0900 hours EDT, for the first two (possibly three) traverses (judging from the minisonde data at Camlachie and Petrolia) the aircraft was probably in relatively stable air, above the mixing layer. It is interesting to note that during this portion of the flight, the ozone measurements aloft were quite patchy (Figure 3(a)), due to scavenging by NO plumes (from generating stations on both sides of the border near Courtright, or possibly other urban/industrial sources in the Sarnia areas). Outside these ozone "dips" caused by NO scavenging, levels in excess of 80 ppb were encoutered aloft. However, at the same time, ground level hourly average ozone values were considerably lower and fairly uniform across the network, at about 45 to 55 ppb. From these observations it is concluded that a significant portion of the rapid ozone increase at ground level during the morning hours of July 14 (Figure 2) was due to mixing downwards of ozone-rich air layers from aloft. Furthermore, although a preliminary glance at Figure 3(a) might suggest the presence of ozone plumes attributable to Sarnia, a closer inspection of the aircraft data indicates that the observed structure in the ozone profiles is largely due to scavenging by $NO_x$ plumes embedded in a reasonably uniform, background air mass, with fairly high ozone loadings (Lusis et al., 1985). In traverses 2 and 3, there is evidence for some ozone buildup over Lake Huron, however, which could possibly be due to air polluted earlier by Sarnia emissions, and carried out over the lake by the early morning southerly winds.

Traverses 4 and 5 (Figures 3(b) and (c)) were flown clear of the Sarnia plume, within the mixing layer. There is now much closer agreement between the aircraft and ground-level ozone measurements, and an indication of an ozone buildup over Lake Erie. It is not clear whether this buildup is due to a Windsor-Detroit plume, or to the occurrence of elevated ozone values in

relatively stable air layers over the water. Over land, ozone concentrations were much more uniform, although the nephelometer and $NO_x$ analyzer data indicate the presence of some residual plumes (possibly from Windsor-Detroit) to the south of Sarnia (Lusis et al., 1985).

The last two traverses, which were carried out downwind of Sarnia (Figure 3(d)), are difficult to interpret. There is evidence of fairly localized ozone buildups due to Sarnia near the southern shoreline of Lake Huron, as well as scavenging by generating station plumes farther to the south. Traverse 7 indicates an appreciable ozone buildup over Lake Huron, but a spiral flown nearby, just after the completion of this traverse, showed that the aircraft had probably intersected a fairly localized high-concentration ozone layer, about 100 m thick, located near the top of a stable air layer over the lake (again, this ozone may have been formed from Sarnia emissions, carried out over the lake on early morning southerly winds).

The hydrocarbon monitoring results on this day are interesting, because the wind was blowing Sarnia emissions towards the Camlachie monitoring site. Hydrocarbon observations at Camlachie, Courtright, and aboard the aircraft are tabulated below, for the periods when there was an overlap of observations from at least two locations.

| Location | Time EDT | Total HC ($C_{3+}$)ug $m^{-3}$ | Alkanes % | Alkenes % | Aromatics % |
|---|---|---|---|---|---|
| Aircraft | 0912-0941 | 84 | 86 | 0.2 | 13 |
| (downwind) | 0943-1013 | 79 | 77 | 0.1 | 22 |
| Courtright | 0854-0954 | 194 | 69 | 2.9 | 21 |
| | 0954-1054 | 149 | 74 | 2.8 | 16 |
| Camlachie | 1048-1148 | 336 | 87 | 3.3 | 8.0 |
| | 1148-1248 | 153 | 81 | 1.2 | 15 |
| Courtright | 1054-1154 | 79 | 81 | 1.0 | 11 |
| | 1154-1254 | 60 | 78 | 1.1 | 10 |
| Aircraft (upwind) | 1018-1048 | 45 | 43 | 0.2 | 56 |

The earlier samples collected aboard the aircraft (downwind, before 1013 hours) and at Courtright (before 1054 hours) are of similar composition, except that the concentration of alkenes is significantly higher at Courtright. In fact, the hydrocarbon levels at Courtright are surprisingly high, even though according to local wind measurements, the Sarnia emissions should have been blown in a northerly to northeasterly direction (away form the site) during the preceding twelve hours or more. The early Courtright measurements resemble the later Camlachie hydrocarbon data, collected between 1048 and 1248 hours, downwind of Sarnia suggesting that upwind (possibly Detroit) emissions may be affecting the entire area.

During the second period, when data are available for Camlachie, both Courtright and the aircraft were collecting samples clear of the Sarnia plume, and observing considerably lower levels than Camlachie. The Camlachie measurements could conceivably have been influenced by the same air parcel that was over Courtright (before 1054), in addition to Sarnia emissions. They show the ambient hydrocarbons to consist largely of alkanes (about 80% by

weight), followed by aromatics (about 10%, roughly one-half being benzene) and alkenes (1-3%). The aircraft samples collected downwind (0912-1013) show considerably lower alkene levels (about one-tenth the percentage of the ground level samples). The aircraft sample collected clear of Sarnia emissions (1018-1048) shows a surprisingly high level of aromatics (56%), and may have been somehow contaminated.

Because of the relatively high levels of alkenes measured at Camlachie during the period 1048-1248, the concurrent $NO_x$ and ozone precursor monitor results were examined. Levels of NOx during the hourly periods 1040 - 1140 and 1140 - 1240 were 0.02 ppm, and below detection limits, respectively: ozone precursor levels were 11 and 18 ppb respectively. Earlier in the day (0854 - 1054), the hydrocarbon levels, and composition of the hydrocarbon mixture, at Courtright was found to be similar to that at Camlachie (1048 - 1248). However, $NO_x$ levels were higher (0.04 and 0.05 ppm during the hours 0849 - 0949 and 0949 - 1049 respectively). It is interesting that the ozone precursor values at Courtright (27 and 25 ppb respectively during the above hours) were considerably higher than the Camlachie ozone precursors, suggesting that in the Sarnia area, oxidant formation may be $NO_x$- limited.

No measurements are available from the York University monitoring site at Camlachie during the period of interest. The TAGA unit at Courtright did collect a reasonably complete set of samples, however, of aldehydes (other than formaldehyde), ketones, acetates and alcohols, indicating levels of 1 - 2 ppb or less, with some compounds (acetone, methanol, propanol) showing occasional excursions in excess of 5 ppb.

In summary, both the aircraft and ground level data on July 14 suggest a contribution from Sarnia to the regional ozone levels, although this contribution is difficult to define. Further, a large ozone reservoir aloft, which may have had a significant contribution from local sources, is suggested in the measurements. This strongly influenced the variation of the ground level ozone concentrations during the morning hours. Although the intensity of solar radiation was not a high on this day as some others, the provincial hourly air quality criterion for ozone was exceeded at most stations in the

study area by late afternoon. The previous air parcel history (from relatively polluted upwind areas) no doubt provides at least part of the explanation for the high regional ozone levels, with Sarnia emissions adding to these.

Table 3 summarizes the observations of ozone and ozone precursor levels, as well as the concurrent meteorological conditions, on all days during the study period when aircraft flights were carried out. This table shows the date and time of measurements (column 1); whether or not there was a measurable Sarnia impact (column 2); the regional ozone levels (column 3); the prevailing meteorological conditions, including 48-hour back trajectories of air parcels in the Sarnia area at the time of the measurements (column 4); ozone precursor measurement results, including hydrocarbon and nitrogen oxide concentration levels at Sarnia in the early morning, and ozone precursor monitor results at Sarnia in the early morning, and ozone precursor monitor results at the time of the aircraft flights (column 5); and other relevant observations, primarily on the quality of the air parcels entering the Sarnia area, as determined from the aircraft concentrations of sulfates and nitrates and light-scattering particulates (column 6).

An examination of Table 3 indicates that on four out of eleven days when aircraft flights were carried out, there was evidence of ozone buildups in the study area due to Sarnia emissions, either as downwind "plumes" (June 28, July 13), or "patches" of elevated ozone levels on the calmer days (July 8 and 14). On these occasions, maximum ozone buildups (over and above "background" levels) of about 20-40 ppb were observed. In agreement with the recently-published observations of Kelly et al., (1986) regarding the impact of Detroit on ozone concentrations in nearby areas in Michigan and Ontario, the plume ozone maxima occurred at some distance from the Sarnia industrial area (about 20-40 km downwind).

It is interesting to note that on some occasions (27 June, 3 July) ozone plumes were also observed from sources upwind of the Sarnia area (although on these days no impact on $O_3$ levels due to Sarnia emissions could be detected).

Thus, on the larger portion of the study days, no impact due to Sarnia emissions could be detected. These included one day (July 13) which approximated the classical "back-of-the-high pressure area" ozone episode, with ozone levels at most stations in the study area exceeding the provincial hourly air quality criterion of 80 ppb. This is not meant to imply that Sarnia hydrocarbon and $NO_x$ emissions do not form atmospheric ozone. There are a number of hydrocarbons in the Sarnia emissions - for example, the alkyl benzenes - which are known to be efficient ozone precursors (Atkinson and Lloyd, 1984). However, during the few hours subsequent to emission that the polluted air parcel remained in the study area, chemical transformation rates and atmospheric dilution were such that measurable ozone buildups apparently did not occur.

On two days when a Sarnia impact was identified (July 13 and 14), and moreover regional ozone levels (as determined from upwind aircraft traverses and monitors clear of Sarnia emissions) were approaching the provincial air quality criterion, the additional ozone produced by Sarnia precursors caused the criterion to be exceeded. The area thus affected was estimated from the data to be on the order of 100-1000 $km^2$, and the duration of the impact on the order of several hours. (It may be noted for comparison that the area of southern Ontario, where exceedences of the provincial air quality criterion for ozone are frequently observed, is on the order of 100,000 $km^2$).

On the two other days when a Sarnia impact was identified, but regional ozone levels were well below the provincial air quality criterion - June 28 and July 8 - no exceedences of the criterion were observed (although on occasion, instantaneous levels in excess of 80 ppb were noted in the aircraft data).

On the basis of these limited observations, it can be concluded that the emissions from Sarnia can on occasion contribute to exceedences of the provincial air quality criterion over limited areas of southwestern Ontario, the affected areas being on the order of 100-1000 $km^2$ in size and occurring within a few tens of kilometers of the Sarnia industrial area. However, on these occasions the maximum observed contributions from Sarnia were about

20-40 ppb above the "background" levels imported into the area, which were frequently well in excess of 40 ppb. Bearing in mind the relatively infrequent occurrence of days when a Sarnia contribution can be detected, the magnitude of the observed contributions and the limited area affected, it is clear that ozone levels in southwestern Ontario are largely governed by the imported component due to long-range transport, rather than generation from local emissions.

With reference to the summary in Table 3, it can be seen that in general no Sarnia impact was observable on the days which were relatively overcast (27 June; 5, 7, 16, 17, 18 July), with the temperatures generally (but not always) on the low side compared to the total set of days, and winds from the westerly quadrant. Air quality and atmospheric visibility in the area were good, because previously the air parcels had passed over areas with few sources of pollution. It is somewhat surprising that no Sarnia impact could be detected on July 3, since high ozone levels were observed in the study area, and an upwind ozone plume had been apparently formed from emissions in the Windsor/Detroit area. The presence of scattered-to-broken clouds on this day, leading to inhibited irradiation, may be of significance.

On the other hand, ozone buildups attributable to Sarnia were observed on several days (8, 13, 14 July) with relatively clear skies and light winds, especially in the morning, when a brown haze layer was noted over the Sarnia area. Temperatures tended to be on the high side compared to the total set of study days, and the atmosphere was somewhat more stable, especially in the morning when low mixing heights were observed (note, however, that relatively low mixing heights also occurred on several days in Table 3 when there was no detectable Sarnia impact on ozone levels). A variety of previous air mass histories was noted, including travel over upwind areas of both low and high emission densities, and this fact was reflected in the overall air quality in the area (e.g. compare July 8, which had good regional air quality and atmospheric visibility, with July 14, when conditions were much more marginal). An exception to the above picture in several respects is 28 June, when fairly brisk westerly winds were encountered, there was no evidence of an early morning stagnation period, and the

mixing layer was quite deep (up to 2000 m). Background air quality was generally good in the study area. Apart from the fact that skies were clear on this day, it is similar in many respects to days in the "no-Sarnia-impact" category (which were overcast), so the impact due to local ozone precursor emissions is evidently very sensitive to the level of insolation.

In a recent paper, Kelly et al. (1986) have presented an extensive discussion of the meteorological conditions associated with ozone buildups in the Detroit Metropolitan area. Since the geographical area here is basically the same as in Kelly et al.'s paper, and Kelly's analysis is based on a relatively large data set, it is interesting to compare the present study's results with the conclusions of Kelly et al. On the basis of a comparison of meteorology and air quality on upper versus lower quartile ozone days, they found that the high ozone days tended to be warmer and sunnier, and had higher barometric pressure and lower wind speeds. Mixing was inhibited on these days, and considerably higher morning pollutant concentrations were noted (in the Detroit Metropolitan area). Strictly speaking, in the above analysis Kelly et al. were not considering the contribution from any specific source area (as in the present study), but rather the total ozone level measured due to a number of upwind contributions. However, their comments are directly relevant as far as the potential for ozone formation from its precursor emissions is concerned, since the upper quartile days are expected to also have a high ozone formation potential. The above meteorological description (Kelly et al., 1986) applies fairly well to 8, 13 and 14 July, when a Sarnia contribution was detected, and one can justifiably generalize that if such conditions occur in southwestern Ontario, then ozone buildups due to Sarnia emissions are highly probable. However, there are other days, such as 28 June, when a Sarnia contribution was also detected, which had clean background air, and even with the Sarnia contribution included, air quality in the study area was good.

A detailed consideration of the atmospheric chemistry, and the question of hydrocarbon vs. $NO_x$ control in the Sarnia area, is beyond the scope of this paper. However, some relevant observations can be made, based on an examination of data collected on the aircraft sampling days.

Firstly, it is interesting to note that, with the exception of June 28 (when the overall air quality in the area was good), hydrocarbon and $NO_x$ levels were relatively high on days when a Sarnia impact on regional ozone was noted, especially in the morning (it must be pointed out, however, that on some others days - 5 and 17 July - when hydrocarbon and $NO_x$ levels were also high, no ozone buildup downwind of Sarnia was detected, presumably because of lack of sufficient sunlight to drive the atmospheric photochemistry). On a number of occasions, significant amounts of alkenes and alkylbenzenes, which are recognized to be ozone precursors, were noted downwind of Sarnia. On 8 July, the aircraft data suggested that the alkylbenzenes may be especially important as far as ozone formation in the Sarnia plume is concerned, but this result must be regarded with caution, since several of the aircraft hydrocarbon samples were suspected to be contaminated. On several occasions elevated levels of aliphatics, which can also form ozone (but on longer time scales - Atkinson and Lloyd, 1984 - and hence not within the study area), were found downwind of Sarnia.

The ozone precursor monitors in general gave high readings when concurrent hydrocarbon and $NO_x$ levels were high, and low readings when they were also low. An interpretation of the ozone precursor monitor results, regarding the question of whether hydrocarbons or nitrogen oxides are the more important ozone precursor in southwestern Ontario, is made difficult by the fact that much of the time $NO_x$ levels were below instrumental detection limits. There is some circumstantial evidence in the data to suggest that in the Sarnia area, oxidant formation may be $NO_x$-limited (see the discussion of the July 14 data, for example). However, this is contradicted by some of the other data (e.g. 8 July), which suggest that hydrocarbons play a controlling role.

Some mathematical modelling runs are also being currently carried out to clarify this question. The basic approach is to use the chemistry module from the ADOM model (Lurmann et al., 1984) together with atmospheric chemistry data collected upwind of the Sarnia area on some of the study days. The "chemical reactor" is then allowed to run for several hours with and

without perturbations in the hydrocarbon and $NO_x$ levels, the hydrocarbon perturbations being determined from the difference between actual upwind and downwind measurements collected during the study. This work is ongoing, but preliminary results are interesting: they suggest that, in the Sarnia area, reactive hydrocarbons injected into the incoming air mass will always lead to downwind ozone production (on sunny summer days). However, the location on the modeled $O_3$ - $NO_x$ - hydrocarbon surface is such, that both increases and decreases in $NO_x$ emissions will result in a reduction of downwind ozone levels.

**Conclusions**

The conclusions below are based on a relatively small data set, which may not be entirely representative of the long-term situation. However, they seem to be consistent with the findings of other investigators who have studied the formation of ozone downwind of urban and industrial areas (see Kelly et al., 1986, as well as the references cited in the Introduction of this paper).

(i) Oxidant precursor emissions from the Sarnia area can lead to the formation of elevated ozone levels downwind. This was observed to occur on four days in the June 27 - July 18 period, out of the eleven days when aircraft flights were carried out. The data suggest that local emissions lead to elevated downwind ozone levels on sunny summer days, especially those with low wind speeds and inhibited atmospheric mixing.

(ii) On these occasions, maximum ozone buildups (above regional background levels) of about 20-40 ppb can be observed. The affected areas can be on the order of 100-1000 $k^2$ in size, and the duration of the impact, several hours. At times, the Sarnia contribution to the total oxidant levels can push hourly ozone concentrations over the provincial air quality criterion of 80 ppb.

(iii) Nevertheless, judging from the frequency of occurrence of ozone buildups attributable to Sarnia emissions, the size of the area affected, and the magnitude of the Sarnia contributions compared to the regional background values, it is clear that ozone levels in southwestern Ontario in the summer are largely governed by the imported component, rather than generation from local emissions.

(iv) A large number of hydrocarbons known to be ozone precursors - especially the alkylated benzenes - can be detected in the air in the Sarnia area, due to emissions at a number of petrochemical industries at Sarnia. However, it is at present not possible to state whether local control measures (should they be necessary) should concentrate on hydrocarbon or $NO_x$ reductions. This is the subject of an ongoing analysis of the air quality measurements, as well as mathematical modelling simulations.

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Table 1

Emission Densities of Hydrocarbons and Nitrogen Oxides in the Sarnia Area*

| Species | Emission Density (metric tons/km²/year) |
|---|---|
| High Reactivity | |
| Alkylbenzenes | 48 |
| > $C_2$ alkenes | 193 |
| Moderate Reactivity | |
| > $C_3$ alkanes | 90 |
| ethylene | 38 |
| Low Reactivity | |
| ethane, propane and benzene | 31 |
| $NO_x$** | 257 |

* Based on a total area of 100 km², comprising sources in the Sarnia urban area, and the petrochemical industries along the St. Clair River within about 15 km of Lake Huron.

** Expressed as $NO_2$.

Table 2
Summary of Air Quality and Meteorological Measurements
Made at Each Monitoring Station and on Aircraft

| | | |
|---|---|---|
| 1. | Windsor | $O_3$, $NO/NO_2/NO_X$, THC[1], RHC[2], $SO_2$, CO, COH[3] |
| 2. | Merlin | $O_3$; anemometer |
| 3. | Bickford | $SO_2$ |
| 4. | Courtright | $O_3$, $NO/NO_2/NO_X$, THC, RHC, $SO_2$, CO, $H_2S$; selected aldehydes, ketones, acetates, alcohols; hydrocarbons by gas chromatography; ozone precursor monitor; anemometer; temp. |
| 5. | Sixth Line | RHC, $C_2H_4$, $SO_2$; anemometer |
| 6. | River Bend | $O_3$, $NO/NO_2$, RHC, $C_2H_4$, $SO_2$; anemometer |
| 7. | LaSalle Road | RHC; anemometer |
| 8. | Scott Road | RHC |
| 9. | River Front | Anemometer |
| 10. | Front Street | $O_3$, $NO/NO_2$, $SO_2$; anemometer |
| 11. | Centennial Park | $O_3$, $NO/NO_2/NO_X$, THC, $SO_2$, CO, COH |
| 12. | Sarnia | $SO_2$; anemometer |
| 13. | Grace Church | $O_3$, $NO/NO_2$, $SO_2$ |
| 14. | Huron View | $O_3$, $NO/NO_2$ |
| 15. | Wyoming | $O_3$ |
| 16. | Thedford | $O_3$ |
| 17. | Parkhill | $O_3$; anemometer |
| 18. | London | $O_3$, $NO/NO_2/NO_X$, $SO_2$, CO, COH, THC |
| 19. | Huron Park | $O_3$ |
| 20. | Grand Bend | Anemometer |
| 21. | Tiverton | $O_3$, $SO_2$, TRS; anemometer; temp. |
| 23. | Camlachie | $O_3$, $NO/NO_2/NO_X$, THC, RHC, $SO_2$, CO, $H_2CO$; $H_2O_2$, hydrocarbons by gas chromatography; ozone precursor monitor; minisonde; anemometer; temp. |
| 24. | Petrolia | Minisonde; acoustic sounder |
| Aircraft | | $O_3$, $NO/NO_X$, $SO_2$, $HNO_3$, particulate $SO_4$ and $NO_3$, THC, visibility (nephelometer), hydrocarbons by gas chromatography |

[1] Total hydrocarbons
[2] Reactive hydrocarbons
[3] Coefficient of haze

Table 3: Summary of Sarnia Oxidant Study Observations

| Date/Time | $O_3$ Observations: Sarnia Impact | $O_3$ Observations: Regional $O_3$ | Meteorology | $NO_x$,HC,$O_3$ Precursor Monitor Observations | Other |
|---|---|---|---|---|---|
| 27 June<br>1300 - 1700 EDT | No, but there was some evidence for an $O_3$ plume from a source upwind of Sarnia | 30-50 ppb | - overcast<br>- brisk W'ly winds (25-36 km $h^{-1}$)<br>- temp. in mid-20's<br>- rel. hum. about 60%<br>- mixing ht. greater than 1000 m<br>- air back trajectories from Nebraska northeastwards to Sarnia | - generally good air quality throughout the day | - upwind:<br>$SO_4$ = 12 ug $m^{-3}$<br>$NO_3$ = 1 ug $m^{-3}$<br>$b_{scat}$ = 1 x $10^{-4}$ $m^{-1}$ |
| 28 June<br>0900 - 1300 EDT | Yes, there was evidence for a downwind plume. The data suggest a delay in $O_3$ formation, no buildup being detected within the first hour or so of air parcel travel time. | 30-40 ppb | - clear<br>- W'ly winds (5-20 km $h^{-1}$)<br>- temp. low to mid-20's<br>- rel. hum. about 50%<br>- max. rad. 94 mw $cm^{-2}$<br>- mixing ht. 600 to 2000 m<br>- air back trajectories from w. edge of Lake Superior, south eastward to central Lake Michigan, then westward to Sarnia | - no early morning buildup of HC, $NO_x$<br>- downwind of Sarnia, HC's were at or below overall survey levels, $NO_x$ generally below detection limits<br>- no downwind $O_3$ precursor monitor measurements were available | - upwind:<br>$SO_4$ = 12 ug $m^{-3}$<br>$NO_3$ = 2 ug $m^{-3}$<br>$b_{scat}$ = 1 x $10^{-4}$ $m^{-1}$<br>$H_2O_2$ about 2 ppb |
| 3 July<br>1000 - 1800 EDT | No, but an $O_3$ plume apparently from the Windsor-Detroit area was observed. | Greater than 80 ppb in afternoon | - back-of-high pressure system<br>- SW winds (10-20 km $h^{-1}$)<br>- temp. mid-to upper 20's<br>- scattered/broken clouds<br>- rel. hum. about 50%<br>- max. rad. 101 mw $cm^{-2}$<br>- mixing ht. greater than 1000 m<br>- air back trajectories follow a northeastward path from Indiana and Illinois | - no early morning HC or $NO_x$ buildup, but relatively high levels of alkanes and aromatics at Camlachie, downwind of Sarnia<br>- no $O_3$ precursor monitor measurements available downwind of Sarnia | - upwind:<br>$SO_4$ = 64 ug $m^{-3}$<br>$NO_3$ = 15 ug $m^{-3}$<br>$b_{scat}$ greater than 2 x $10^{-4}$ $m^{-1}$ |

Table 3: Summary of Sarnia Oxidant Study Observations (Cont'd)

| Date/Time | $O_3$ Observations: Sarnia Impact | $O_3$ Observations: Regional $O_3$ | Meteorology | $NO_x$, HC, $O_3$ Precursor Monitor Observations | Other |
|---|---|---|---|---|---|
| 5 July<br>0900 - 1300 EDT | No | Generally less than 60 ppb | - broken to overcast cloud cover<br>- light and variable winds<br>- temp. near 20°C<br>- rel. hum. 60-70%<br>- max. rad. 70 mw $cm^{-2}$<br>- mixing ht. 200-500 m<br>- air back trajectories from Illinois, northeastward to lower Lake Michigan, then eastward to Sarnia | - generally high HC's (mainly alkanes and aromatics)<br>- $O_3$ precursor monitor levels up to 16 ppb | - upwind:<br>$SO_4$ = 75 ug $m^{-3}$<br>$NO_3$ = 8 ug $m^{-3}$<br>(possibly due to an imported plume) |
| 7 July<br>0900 - 1300 EDT | No | Less than 40 ppb | - cloudy<br>- W - NW winds (20-25 km $h^{-1}$)<br>- temp. 13 - 15°C<br>- rel. hum. 50-60%<br>- max. rad. 60 mw $cm^{-2}$<br>- morning mixing layers at less than 700 m, stable in afternoon<br>- air back trajectories from North Ontario | - low HC, $NO_x$ levels throughout the area<br>- $O_3$ precursor measurements below detection limits | - upwind:<br>$SO_4$ = 6 ug $m^{-3}$<br>$NO_3$ = 0.8 ug $m^{-3}$<br>$b_{scat}$ less than $0.5 \times 10^{-4}$ $m^{-1}$ |
| 8 July<br>0800 - 1900 EDT | Pockets of elevated $O_3$ concentrations in morning. Relatively high $O_3$ observed at some intermediate ground-level sites in afternoon. | Less than 30 ppb in morning. About 40 ppb in afternoon | - clear<br>- light and variable winds<br>- lake breeze in afternoon<br>- temp. low to mid-20's<br>- rel. hum. 40-50%<br>- max. rad. 100 mw $cm^{-2}$<br>- mixing ht. between 150-800 m throughout day<br>- air back trajectories from west Lake Superior, southeastward across central Lake Michigan | - relatively high early morning $NO_x$, HC (alkanes, benzene, alkylbenzenes) levels<br>- however, $O_3$ precursor data were found to be low<br>- aircraft HC data suggest that alkylbenzenes may be an important $O_3$ precursor | - brown haze in morning over Sarnia<br>- upwind:<br>$SO_4$ = 6 ug $m^{-3}$<br>$NO_3$ = 2 ug $m^{-3}$<br>$b_{scat}$ less than $0.5 \times 10^{-4}$ $m^{-1}$ |

Table 3: Summary of Sarnia Oxidant Study Observations (Cont'd)

| Date/Time | $O_3$ Observations: Sarnia Impact | $O_3$ Observations: Regional $O_3$ | Meteorology | $NO_X$, HC, $O_3$ Precursor Monitor Observations | Other |
|---|---|---|---|---|---|
| 13 July<br>0800 - 1700 EDT | Yes, there was evidence for a downwind $O_3$ plume, with maximum concentrations about 20-40 km from Sarnia | 30-40 ppb in morning.<br>50-70 ppb in afternoon. | - relatively clear<br>- light winds (5-15 km $h^{-1}$)<br>- lake breeze<br>- temp. in mid-upper 20's<br>- rel. hum. 50-60%<br>- max. rad. 103 mw $cm^{-2}$<br>- mixing ht. 100-1000 m in morning<br>- air back trajectories from west Wisconsin, southeast and central Lake Michigan | - $NO_X$, HC (alkanes, alkylbenzenes) relatively high in early morning<br>- relatively high $O_3$ precursor monitor values (20 ppb) | - brown haze in morning over Sarnia<br>- upwind:<br>$SO_4$ = 6 ug $m^{-3}$<br>$NO_3$ = 2 ug $m^{-3}$<br>$b_{scat}$ less than 1 x $10^{-4}$ $m^{-1}$ |
| 14 July<br>0900 - 1200 EDT | A Sarnia impact is suggested in the aircraft and ground level data | Rapidly increasing in morning. Greater than 80 ppb at most stations by late p.m. Large $O_3$ reservoir aloft during morning. | - scattered clouds<br>- southwesterly winds (10-20 km $h^{-1}$)<br>- temp. in mid-upper 20's<br>- rel. hum. 50-60%<br>- max. rad. 80 mw $cm^{-2}$<br>- morning mixing ht. 150-1000 m<br>- air back trajectories from Illinois northeastward | - relatively high morning levels of alkenes, aromatics, at Courtright, Camlachie<br>- urban HC and $NO_X$ levels were not abnormal<br>- relatively high $O_3$ precursor monitor values (up to 27 ppb) | - brown haze in morning over Sarnia<br>- upwind:<br>$SO_4$ = 54 ug $m^{-3}$<br>$NO_3$ = 20 ug $m^{-3}$<br>$b_{scat}$ greater than 1 x $10^{-4}$ $m^{-1}$ |
| 16 July<br>0800 - 1300 EDT | No | Less than 45 ppb. | - broken clouds<br>- W - NW winds (20-25 km $h^{-1}$)<br>- temp. low 20's<br>- rel. hum. 50-60%<br>- max. rad. 100 mw $cm^{-2}$<br>- mixing ht. 400-600 m<br>- air back trajectories from Manitoba southeastwards | - relatively low HC, $NO_X$ levels<br>- $O_3$ precursor levels below detection limits | - upwind:<br>$SO_4$ = 4 ug $m^{-3}$<br>$NO_3$ = 1 ug $m^{-3}$<br>$b_{scat}$ less than 0.5 x $10^{-4}$ $m^{-1}$ |

Table 3: Summary of Sarnia Oxidant Study Observations (Cont'd)

| Date/Time | $O_3$ Observations: Sarnia Impact | $O_3$ Observations: Regional $O_3$ | Meteorology | $NO_X$, HC, $O_3$ Precursor Monitor Observations | Other |
|---|---|---|---|---|---|
| 17 July<br>0800 - 1100 EDT | No | Less than 60 ppb (daily max.) | - overcast<br>- SW'ly winds (15-20 km $h^{-1}$)<br>- temp. low 20's<br>- rel. hum. 60-70%<br>- rad. at time of flight 30 mw $cm^{-2}$<br>- mix. ht. zero to 500 m<br>- air back trajectories from north Michigan, to lower Lake Michigan, then NE to Sarnia | - relatively high HC, $NO_X$, due to low mixing height at time of sampling<br>- $O_3$ precursor monitor at 11-20 ppb | - upwind:<br>$b_{scat}$ = 0.5 x $10^{-4}$ $m^{-1}$<br>no $SO_4$, $NO_3$ data |
| 18 July<br>1100 - 1300 EDT | No | Less than 45 ppb | - overcast<br>- NW'ly winds (20 km $h^{-1}$)<br>- temp. in upper teens<br>- rel. hum. 60-80%<br>- rad. 60-80 mw $cm^{-2}$<br>- mix. ht. 400-800 m<br>- air back trajectories from central Minnesota through Lake Michigan SE to Sarnia | - relatively low HC, $NO_X$ levels<br>- $O_3$ precursor monitor levels below detection limits | - upwind:<br>$SO_4$ = 17 ug $m^{-3}$<br>$NO_3$ = 2 ug $m^{-3}$<br>$b_{scat}$ = 0.5 x $10^{-4}$ $m^{-1}$ |

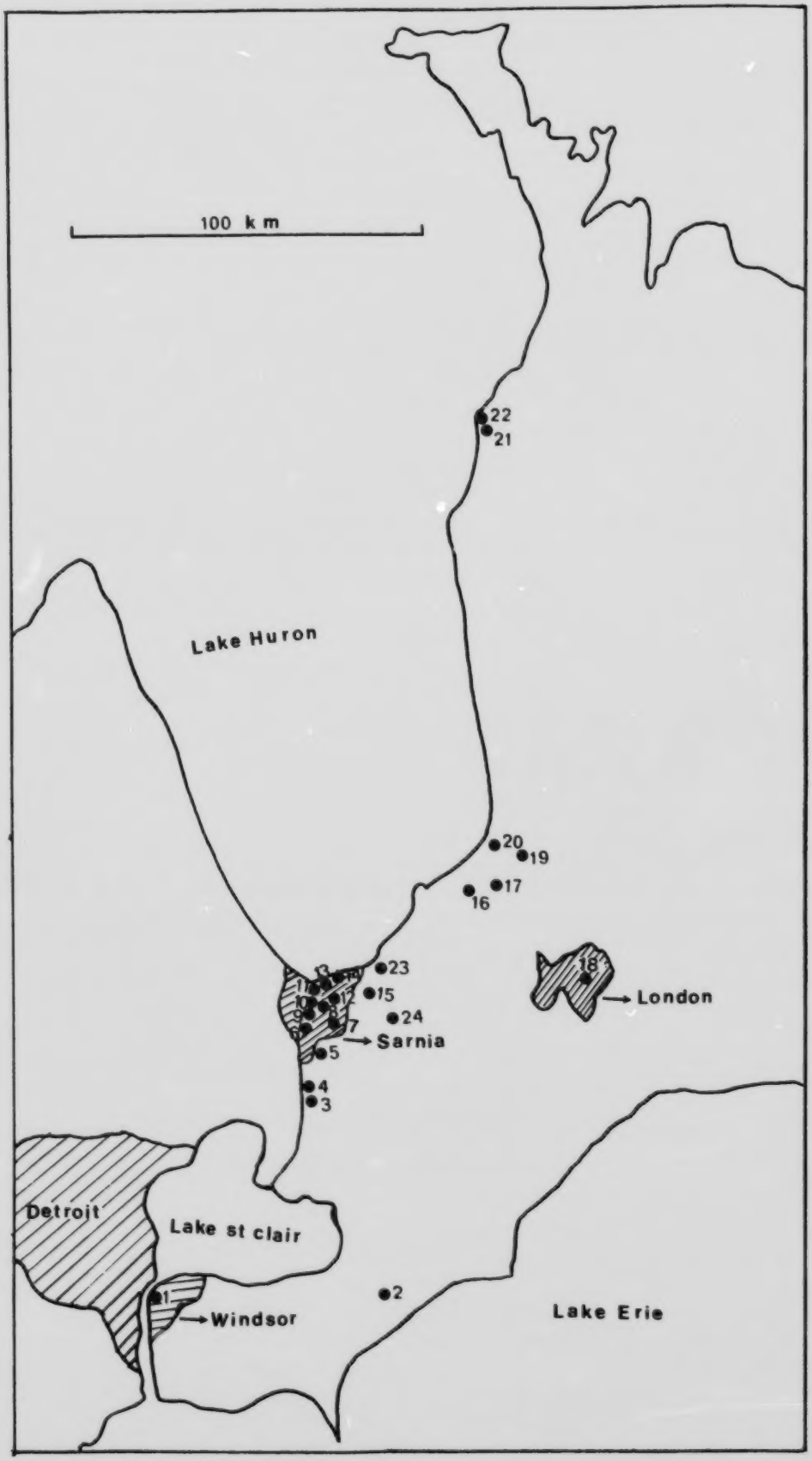
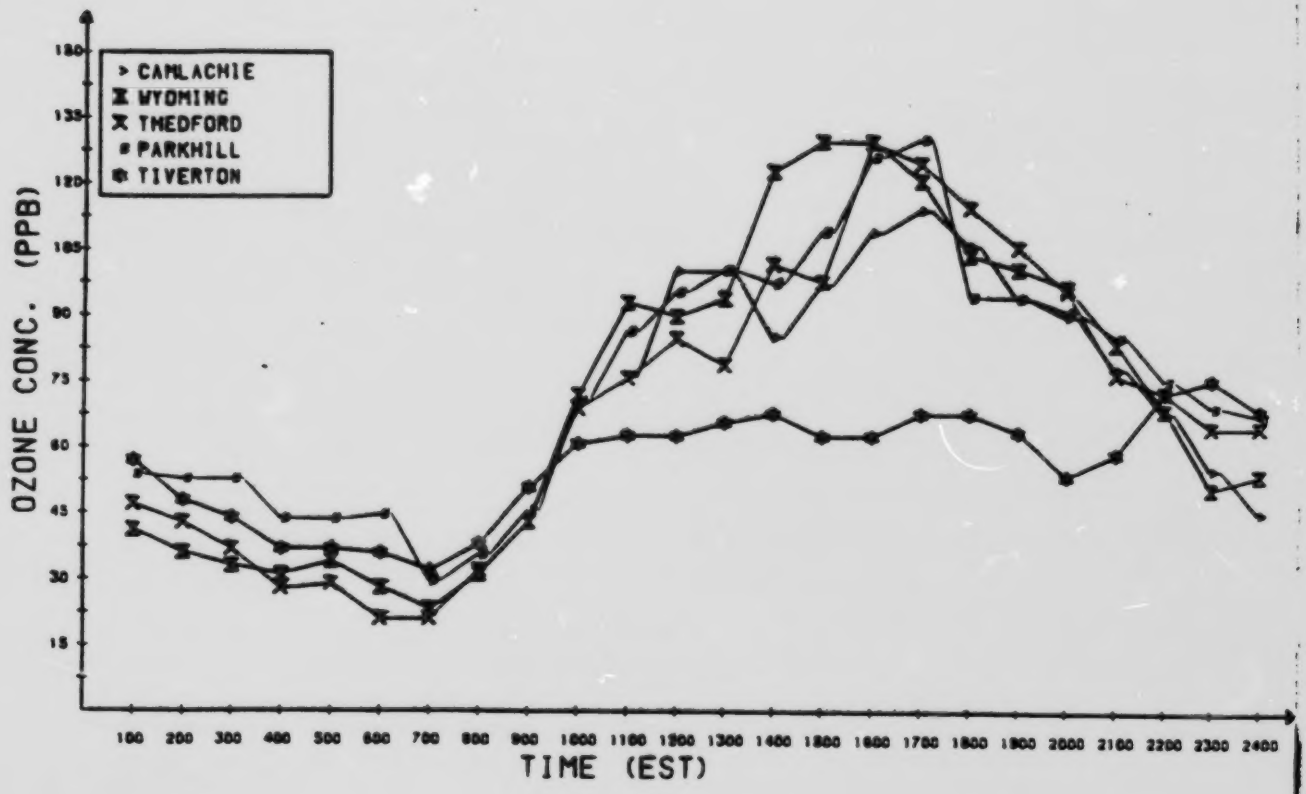



Figure 1: Location of Air Quality and Meteorological Monitoring Sites.

## TIME VS. OZONE CONCENTRATION





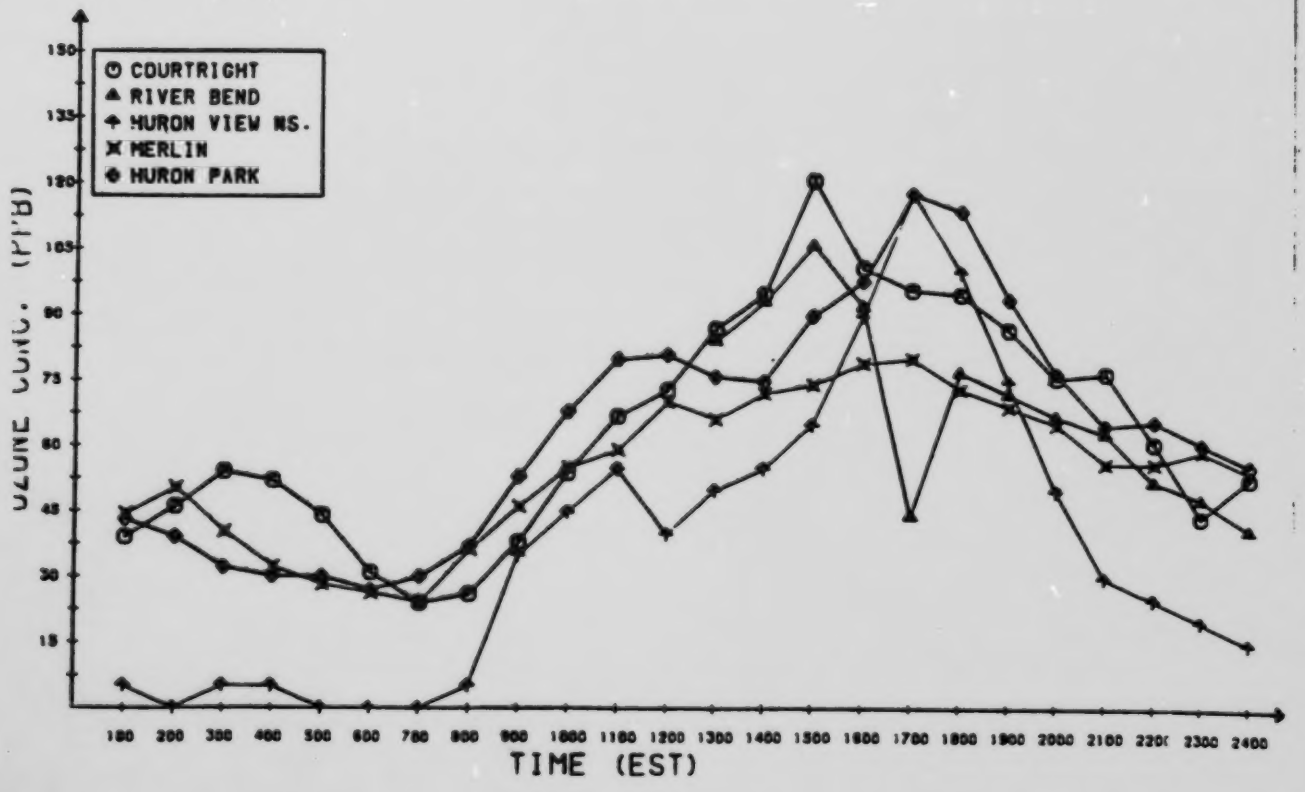




**Figure 2:** **Diurnal Variation of Ozone Concentrations in the Sarnia Area, July 14**

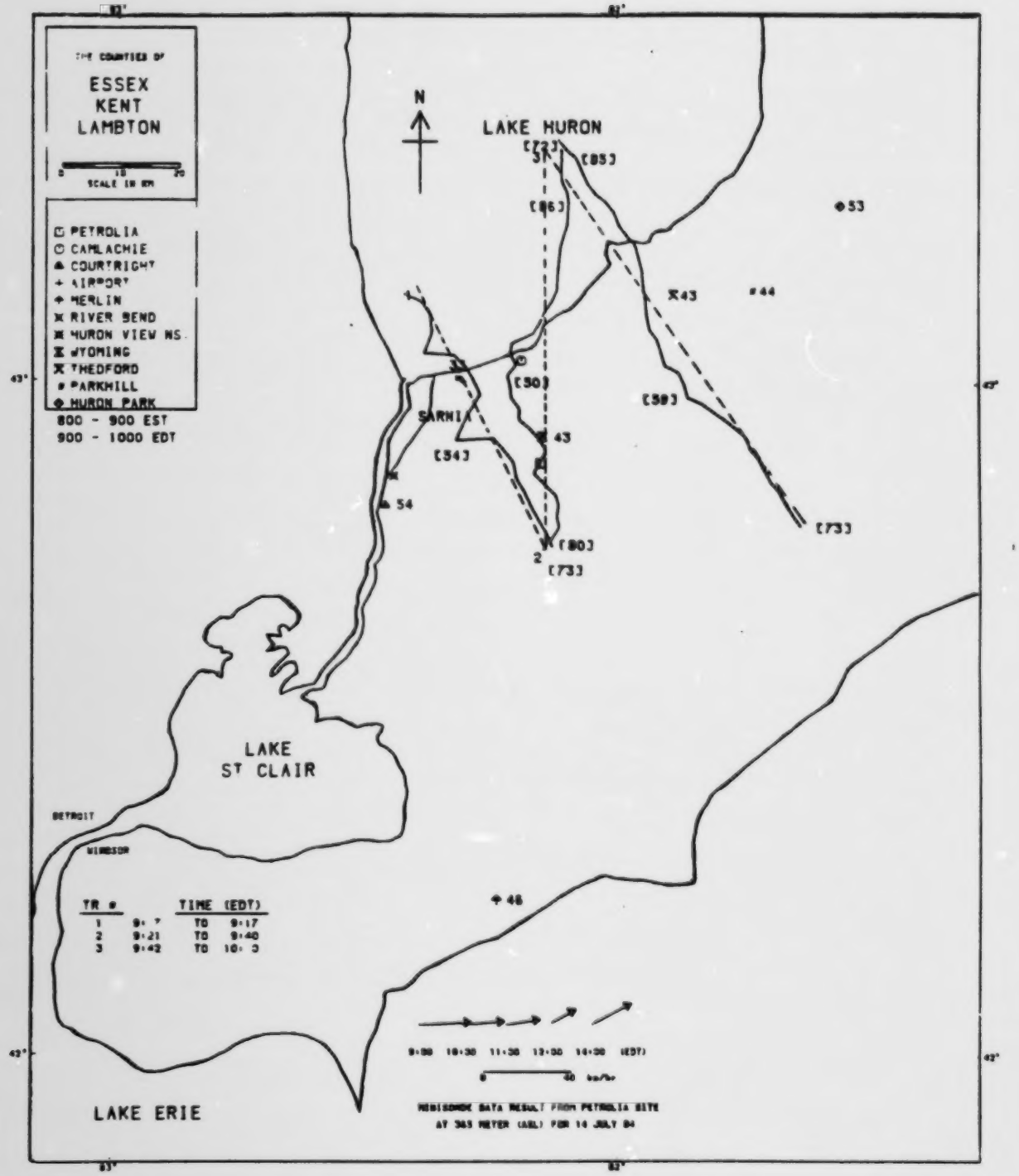



**Figure 3 (a): Ozone Observations in the Sarnia Area on July 14, 9-10 EDT**

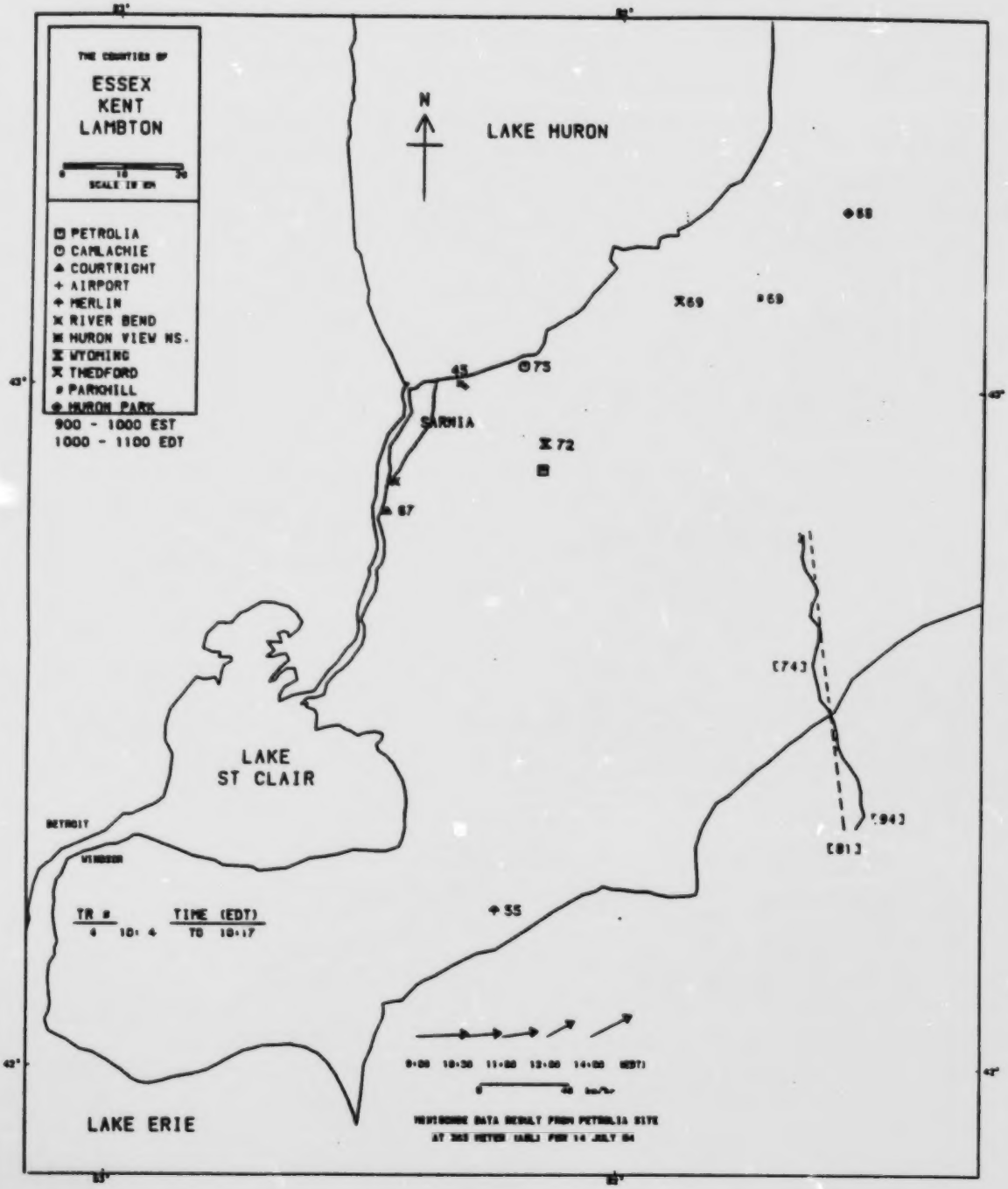



**Figure 3 (b): Ozone Observations in the Sarnia Area on July 14, 10-11 EDT.**

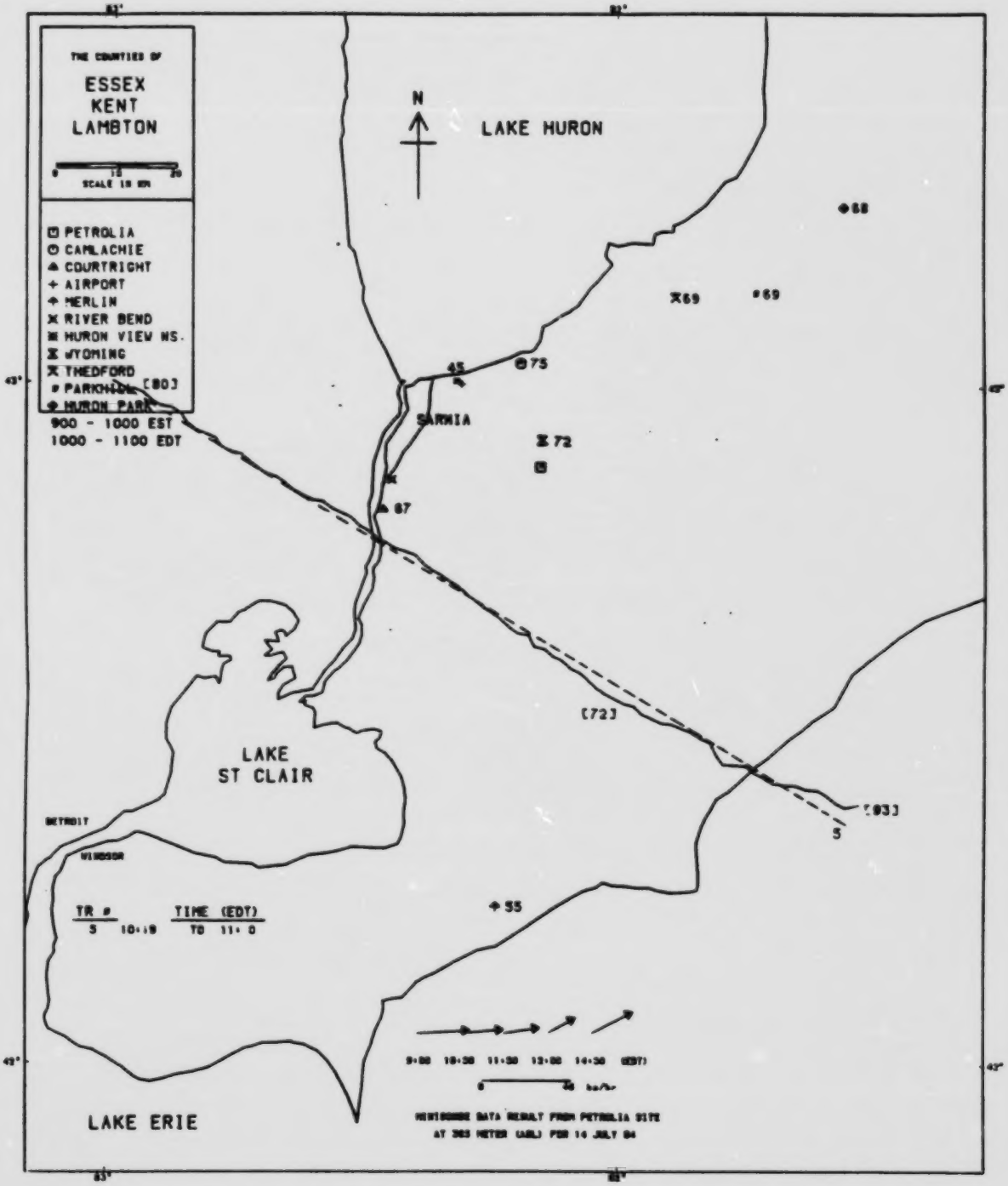



**Figure 3 (c): Ozone Observations in the Sarnia Area on July 14, 10-11 EDT (continued)**

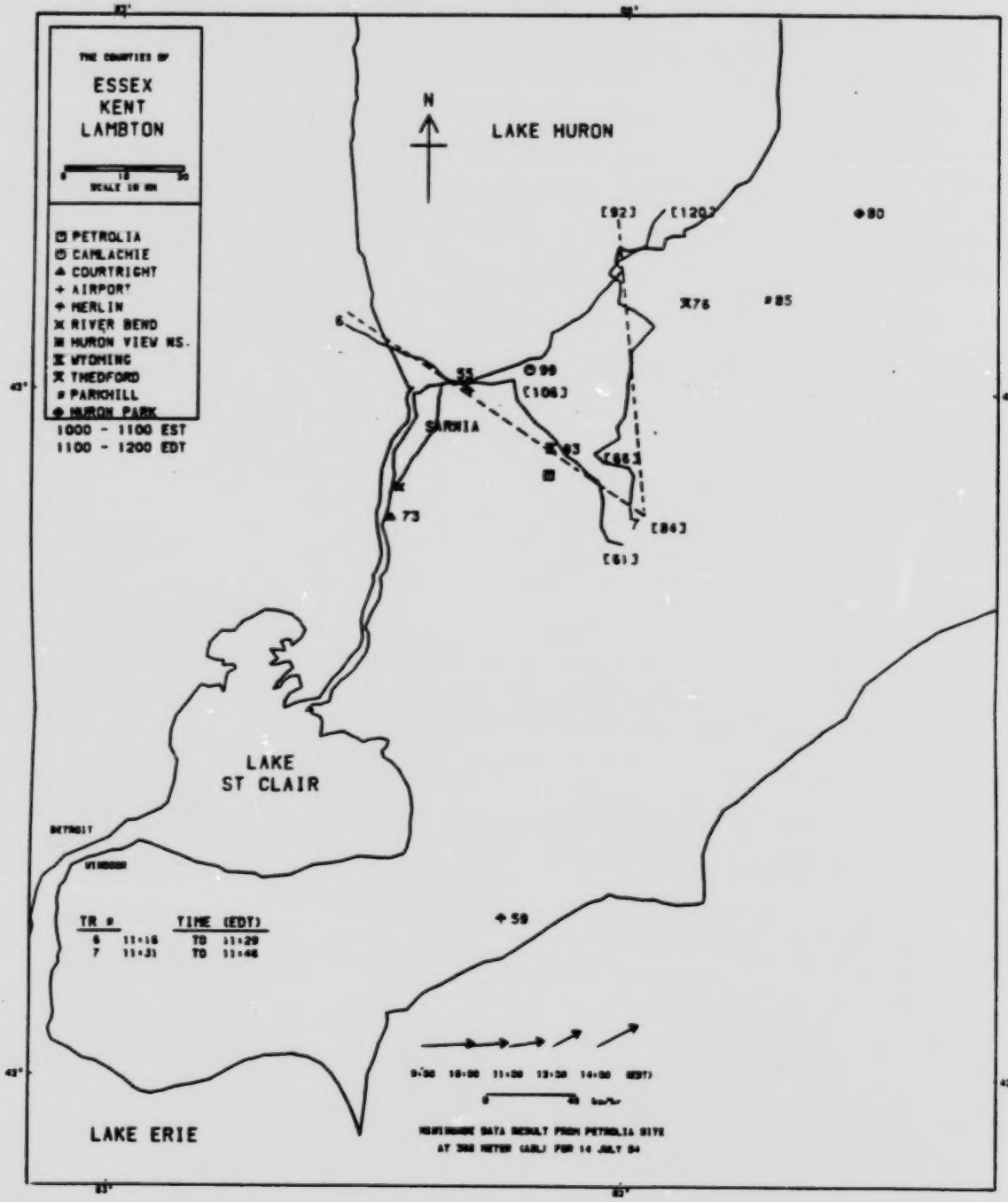



**Figure 3 (d): Ozone Observations in the Sarnia Area on July 14, 11-12 EDT**

## QUATRIÈME SÉANCE/SESSION IV

## SURVEILLANCE DES OXYDANTS/OXIDANT MONITORING

Président/Chairman

Jean A. Roy
Directeur général du milieu atmosphérique
Ministère de l'Environnement du Québec

# THE MEASUREMENT OF OXIDANT PRECURSORS AND THEIR RELATIONSHIP TO OZONE FORMATION

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## RÉSUMÉ

Au cours des périodes d'été de 1984 à 1986, on a effectué des mesures des oxydes d'azote et du carbone organique autre que le méthane (NMoC) entre six heures et neuf heures a.m. dans diverses villes des États-Unis. Dans toutes les villes échantillonnées, le taux d'ozone dépasse la norme de 0,12 ppm émise par le Bureau des normes nationales sur la qualité de l'air ambiant (NAAQS). De ces échantillons, 10 à 20 pour cent ont servi à exécuter des mesures plus détaillées du NMOC. Le présent exposé présente les données sur le NMOC pour les 19 sites échantillonnés au cours de l'enquête de 1985. Ces données sont utiles à la fois pour l'élaboration de modèles photochimiques sur l'ozone et pour l'évaluation des sources contribuant aux concentrations atmosphériques ambiantes. Il semble que ce soit le NMOC qui a le plus d'incidence sur la formation de l'ozone lorsque les ratios NMOC: $NO_x$ sont faibles.

# The Measurement of Oxidant Precursors and Their Relationship to Ozone Formation

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## Abstact

During the summer periods of 1984 through 1986 measurement of 0600 to 0900 AM nonmethane organic carbon (NMOC) and nitrogen oxides ($NO_x$) were made at various cities throughout the United States. The cities sampled all experience ozone levels above the U.S. National Ambient Air Quality Standard (NAAQS) of 0.12 ppm. Detailed NMOC measurements were performed on approximately 10 to 20% of the samples collected. This paper presents speciated NMOC information for the 19 sites sampled during the 1985 study. Speciated NMOC information is useful for both the development of photochemical ozone models and the evaluation of sources contributing to the ambient air concentration. It appears that NMOC composition has the greatest impact on ozone formation at the lower NMOC to $NO_x$ ratios.

## INTRODUCTION

Measurement of nonmethane organic carbon (NMOC) compounds and nitrogen oxides ($NO_x$) during the 0600 to 0900 AM period was conducted at several urban areas throughout the United States from 1984 through 1986. The urban areas studied all have been identified as non-attainment areas of the United States National Ambient Air Quality Standard (NAAQS) for ozone (Federal Register, 1983). By law the States in which these cities are located are required to provide precursor control strategy to bring these areas into ozone attainment. These control plans are referred to as State Implementation Plans (SIP). Current control strategy guidance relate afternoon ozone concentrations to 0600 to 0900 AM precursor levels (EPA, 1981). Previously states used continuous total hydrocarbon analyzers to measure ambient air NMOC concentrations. These analyzers, however, have been shown to be inaccurate and unreliable for NMOC measurements at ambient air concentrations (McElroy 1975, Harrison 1977, and Richter 1983). A new approach was offered to the states to measure NMOC accurately at concentrations below 100 ppbC. This approach involved the cryogenic preconcentration of ambient air prior to injection into a flame ionization detector (FID) and is referred to as a preconcentration direct flame ionization detector (PDFID) (McElroy 1986). The measurement approach removes air and methane from the air sample permitting direct determination of NMOC.

In the cities studied samples were collected in stainless steel containers and shipped to a central laboratory located at the Research Triangle Park, North Carolina for analysis (McElroy 1985). Approximately 10 to 20% of the air samples were selected for detailed gas chromatographic analysis. The GC analyses were used for both quality assurance (QA) of the PDFID procedure and to determine NMOC composition in the urban area studied. A diversity of cities were

studied that included those dominated by vehicular traffic while other areas contained major petrochemical sources. The NMOC compositional measurements determined in these studies will be useful in the development of the chemical mechanisms used in ozone photooxidation models and to perform sensitivity tests to determine models accuracy for ozone predictions.

To date 36 cities have been sampled during the 3-year period from 1984 to 1986. The purpose of this paper is to present and compare the NMOC results obtained in some of the cities studied. The NMOC results from the 1985 Nineteen City Study were selected for presentation in this report.

## EXPERIMENTAL

The sample collection device and the PDFID system used for these studies have been published elsewhere (McElroy 1985). The publication contains detailed information concerning the sample canisters, the sample collection device, and the PDFID analysis system.

Details of the GC system and the preconcentration procedure have been published elsewhere (Seila 1986). The column used was a 60m x 0.32 mm i.d. DB-1 fused silica column (J&W Scientific, Cordova, CA). The helium carrier gas flowrate was maintained at 2 to 3 $cm^3$ $min^{-1}$. The column temperature conditions consisted of an initial 1 min hold at -50°C followed by temperature programming at 8°C/min to a final temperature of 200°C with a final hold time of 5 min. Calibration of the individual compound peaks was performed with a National Bureau of Standards (NBS) 2.84 ppm propane in air Standards Reference Material (SRM) No. 1665b cylinder. A single response factor was used to determine all GC peak concentrations. This approach has been determined to be valid for most hydrocarbon compounds (Deitz 1967). Canister samples were generally analyzed on the GC system within 2 to 4 days after collection.

At least one sample from each city studied was re-analyzed with chemical stripper columns (Klosterman 1967, Lonneman 1983). A 10 cm X 1.25 cm stainless steel column packed with mercuric sulfate-sulfuric acid mixture coated on 40-60 mesh Chromasorb P was used to remove olefinic hydrocarbon peaks from the air sample. A similar 10 cm X 1.25 cm stainless steel column packed with silver sulfate-sulfuric acid mixtrue on 40-60 mesh Chromasorb P was used to remove all aromatic peaks except benzene which is approximately 60% removed.

## RESULTS AND DISCUSSION

The urban sites included in the 1985 Nineteen City Study are listed in Table I. Actually only 18 cities were studied since 2 sites were located in Philadelphia. Eight of the cities studied were located in the state of Texas with 5 of these cities situated on the industrialized southeast coast of the state. Two criteria were used in the selection of samples for GC speciation analysis. First, the selected samples for all sites were equally distributed over the entire sampling period. An attempt was made to select an equivalent number of Monday, Tuesday, Wednesday, Thursday, and Friday samples to avoid possible day-of-week bias. Second, samples collected at sites that experienced afternoon ozone which exceeded 0.12 ppm were selected. It was anticipated that the GC analyses for high ozone days would be particularly useful to the states for their modeling studies. The latter criteria may have resulted in a biased high average NMOC concentration for the GC samples at these sites since usually high precursor concentration are observed on days of high afternoon photochemical ozone levels. However, NMOC emission patterns are expected to be somewhat consistent on a day to day basis. Consequently NMOC composition is not expected to be significantly different on these high ozone days.

Figure 1 shows a comparison of mean NMOC concentration by site for all samples analyzed with the PDFID procedure with those selected for detailed GC analysis. The general comparability between the two measurement procedures is quite reasonable. The two sites that show significant disagreements are the Philadelphia sites 13 and 14. The GC means are approximately 25% higher than the PDFID means. For these two sites during the 1985 study pre-selection sample bias may be a legitimate explanation. Several samples were analyzed as the result of high afternoon ozone levels observed in the Philadelphia area. The mean NMOC levels observed at these sites range from approximately 0.40 ppmC at Boston, MA to about 1.8 ppmC at Beaumont, Texas.

The number of GC peaks observed at the sites ranged from about 100 on low NMOC concentration days to more than 240 peaks on the higher NMOC concentration days. Currently 65 of the GC peaks have been identified and verified by retention time location using pure hydrocarbon compounds. Consequently for high NMOC samples more than 175 GC peaks remain unidentified. In an effort to determine some information of these peaks, selected samples were re-analyzed using stripper columns selective for the removal of olefinic and aromatic compounds (Klosterman 1967, Lonneman 1983). Using this approach on assignment of the unidentified peaks as paraffinic, olefinic and aromatic could be made. At least one pair of stripper column analyses were performed for each urban site sampled in 1985. No surprises were experienced by comparison of stripper column results from site to site. The same paraffin, olefin, or aromatic identifications were assigned to the similar retention time unknown peaks observed in the different cities. Using the hydrocarbon classification assignments determined from the stripper column analyses, bar charts of known and unknown paraffins, olefins, and aromatics are presented respectively for each site in Figures 2, 3,

and 4. As can be observed from the figures, the majority of the hydrocarbon mass for each hydrocarbon classification group is accounted for as known hydrocarbon compound. This demonstrates that the unknown peaks, even though more abundant than known peaks, have quite low ambient air concentrations. Reviewing the results in Figures 2, 3, and 4 indicates that a larger percentage of the aromatic comppound mass is unknown compared to the paraffinic and olefinic compounds. The reason for this is that the largest unknown peaks have been tentatively identified as aromatic compounds. From Figures 2, 3, and 4, it appears that the Beaumont, Texas site has the highest average percentage of unknown compound mass of any of the 19 sites sampled in 1985.

Determination of the sources contributing to the NMOC levels observed in the cities studied is quite a difficult task since similar hydrocarbon compounds are released by vehicular and industrial sources. Source hydrocarbon compositions have been utilized in an effort to characterize NMOC composition in urban ambient air (Mayrsohn 1976, Scheff 1986). These procedures have been somewhat successful in the evaluation of source contribution, however, many more source compositional measurements are required to further develop these techniques. An approach to characterize NMOC source contribution is the use of acetylene as a tracer of vehicular tailpipe emissions. Acetylene is nearly unique to the vehicular combustion process except in those urban areas where it is manufactured or is used in industrial processes. Also acetylene possesses a long atmospheric lifetime of approximately 150 days which is important for its use as a vehicular tracer. To utilize acetylene as a tracer, a source area dominated by vehicular traffic is required. A tunnel was selected as the sampling location since it is dominated by vehicular tailpipe emissions. It is also thought

that the tunnel atmosphere is representative of a large number of vehicles and fuel types used in typical urban areas. Ratios of NMOC compounds and sum of NMOC compounds to acetylene were determine in the Lincoln Tunnel (Lonneman 1986). Some of the ratios determined are shown in Table II. To calculate estimated vehicular concentrations the average acetylene concentration observed at a site is multiplied by the ratios given in Table II. These calculations were performed for the sum of paraffins, olefins, and aromatics at the cities studied in 1985 and are given in Figures 5, 6, and 7. Significant non-vehicular paraffin sources are observd in all cities as shown in Figure 5. Typically the vehicular paraffin estimate at most sites is 50% or less of the total paraffins. This relatively low vehicular contribution of the paraffins is not surprising since significant concentrations of ethane and propane from natural gas and n-butane and isopentane from gasoline evaporative sources are generally observed in most urban areas studied. More than 90% of the paraffins measured at Beaumont, TX are from non-vehicular sources. Review of Figure 6 suggests that 90% or greater of the total olefins at most sites can be accounted for from vehicular sources. Non-vehicular olefins sources are however observed at the Beaumont, Clute, Houston, Orange, and Texas City, TX sites. Beaumont, TX again shown the most abundant non-vehicular olefin sources. In Figure 7 it appears that significant non-vehicular aromatics are suggested for many of the cities. However at 5 of the 19 sites vehicular contribution exceeds 80%.

Comparison of paraffin, olefin, and aromatic compositions at the 19 sites are shown in Figure 8. Typically the paraffins are the most abundant species of hydrocarbon at all sites ranging from 45 to 60% of the total NMOC. Aromatic hydrocarbons are generally

the next most abundant hydrocarbon type ranging from 20 to 30% of total NMOC. Olefins are the least abundant class of hydrocarbon ranging from 15 to 20% of total NMOC. This general compositional breakdown, however, is not observed at the industrial-urban sites on the southeast coast of Texas. At Beaumont, TX (Site 1) and Clute, TX (Site 5) the olefin content is significantly greater than the aromatic fraction. Ozone formation from such a diversity of NMOC composition are expected to be quite different. To test this hypothesis, 12 hour photochemical ozone model simulations were performed using the carbon bond (CB) IV chemical mechanism for three urban areas with drastically different NMOC compositions. Table III contains the compositional breakdown of Beaumont, TX, Washington, DC, and Lake Charles, LA in CB (IV) notations. Beaumont, TX was selected because of its high paraffinic content which resulted in the largest PAR fraction observed among the 19 sites studied in 1985. High olefinic content of the NMOC measured at Beaumont also resulted in an OLE fraction that too was larger than any of the other 18 sites. Highest aromatic content was observed at Washington, DC and resulted in the highest TOL and XYL fraction observed at the 19 sites. The NMOC composition at Lake Charles, LA contained the largest contribution of nonreactive compounds observed at the 19 sites and consequently the largest NR fraction. Simulations at NMOC to $NO_x$ ratios of 6, 12, and 24 to 1 were performed. Initial conditions and other input parameters used for these simulations are given in Table III.

Ozone profiles of the 12 simulation results are given in Figures 9, 10, and 11. At the lowest NMOC to $NO_x$ ratio (Figure 9), a significant difference is observed between Lake Charles ozone profile and the profiles determined at the other two sites. The large NR fraction at Lake Charles has significantly reduced ozone

maximum and increased the time when ozone maximum is observed. Some small differences are observed between the Beaumont, TX and Washington, DC profiles, however, the overall reactivity of the two NMOC compositions appear to be comparable. As the NMOC to $NO_x$ ratios are increased (Figures 10 and 11), differences in the ozone profiles seem to disappear. This is particularly true in the case at the 24 to 1 ratio (Figure 11) where the ozone profiles at all three sites appear to intertwine. Applying these results to the ambient air suggest that NMOC reactivity is more important at lower NMOC to $NO_x$ ratios.

## CONCLUSIONS

Conclusions of the NMOC results measured in the 1985 Nineteen Cities Study are three-fold. First, the largest GC peaks observed in these cities have been identified consequently the largest fraction of NMOC mass is known. Secondly, hydrocarbon compositional information is quite useful for the evaluation of source contribution and ultimately to the control of hydrocarbon precursors. Lastly, hydrocarbon compostion appears to have a greater effect on ozone formation at lower NMOC to $NO_x$ ratios.

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TABLE I

Site Identifications For The 1985 Nineteen City Study

| Site ID | Site Abbreviation | Site Number |
|---|---|---|
| Beaumont, TX | BMTX | 1 |
| Boston, MA | BOMA | 2 |
| Baton Rouge, LA | BRLA | 3 |
| Cleveland, OH | CLOH | 4 |
| Clute, TX | CLTX | 5 |
| Dallas, TX | DLTX | 6 |
| El Paso, TX | ELTX | 7 |
| Fort Worth, TX | FWTX | 8 |
| Houston, TX | HSTX | 9 |
| Kansas City, MO | KCMO | 10 |
| Lake Charles, LA | LCLA | 11 |
| Orange, TX | ORTX | 12 |
| Philadelphia, PA (1) | A1PA | 13 |
| Philadelphia, PA (2) | P2PA | 14 |
| Portland, ME | PTME | 15 |
| Richmond, VA | RVA | 16 |
| St. Louis, MO | SLMO | 17 |
| Texas City, TX | TCTX | 18 |
| Washington, DC | WDC | 19 |

TABLE II

Selected NMOC Compound and Sum of NMOC Compounds to
Acetylene Ratios Determined from the 1982 Lincoln Tunnel Study

| Component | Ratio |
|---|---|
| n-Butane | 1.21 ± 0.19 |
| Toluene | 1.89 ± 0.13 |
| Propene | 0.78 ± 0.08 |
| Sum of Paraffins | 10.53 ± 1.30 |
| Sum of Olefins | 6.03 ± 0.63 |
| Sum of Aromatics | 9.58 ± 0.73 |
| Sum of NMOC | 26.0 ± 2.10 |

TABLE III

Carbon Bond IV Fractions for Three 1985 Cities and Other
Model Input Conditions for 12 Hour Photooxidation Simulations

| CB IV Fraction | Beaumont, TX | Washington, DC | Lake Charles, LA |
|---|---|---|---|
| OLE | 0.076 | 0.031 | 0.017 |
| PAR | 0.656 | 0.523 | 0.589 |
| TOL | 0.067 | 0.132 | 0.070 |
| XYL | 0.057 | 0.132 | 0.073 |
| HCHO | 0.021 | 0.022 | 0.021 |
| ALD2 | 0.034 | 0.055 | 0.048 |
| ETH | 0.023 | 0.039 | 0.018 |
| NR | 0.068 | 0.070 | 0.172 |

Model Input Conditions

Mixing Height Rise from 250 to 1235 meters
Los Angeles Summer Solstice
Ozone Aloft was 0.05 ppm
Temperature was 303°A
$H_2O$ was 25,000 ppm (50% RH)
Initial $NO_x$ Composition was 75% NO and 25% $NO_2$
Simulation Time Period 8 AM to 8 PM

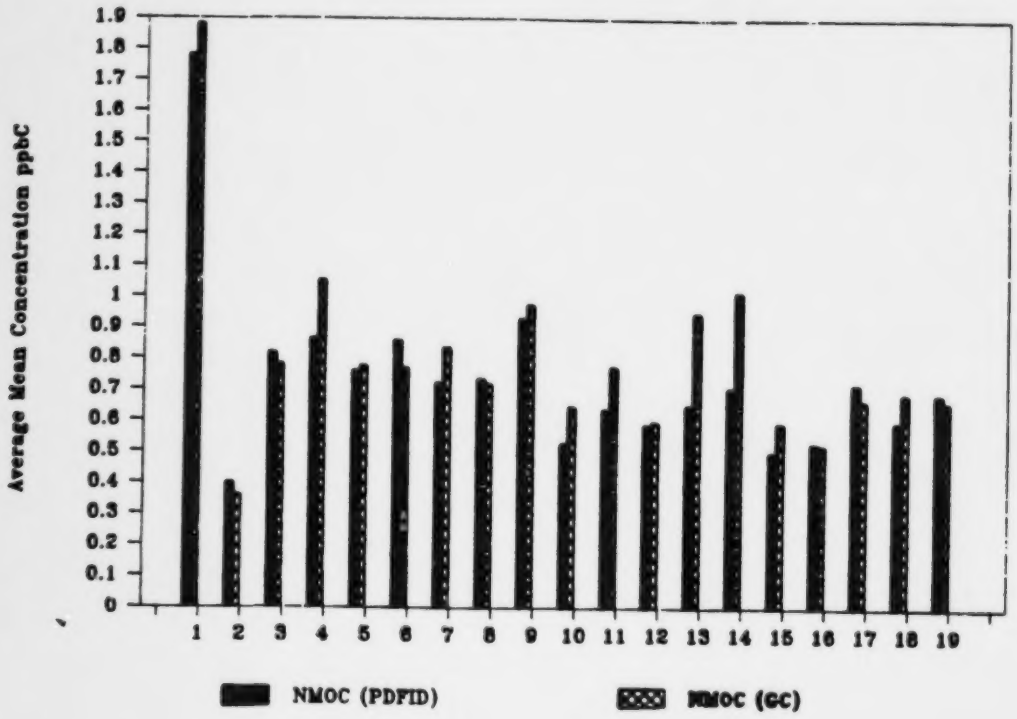


Figure 1. Comparison of average mean concentration obtained with the PDFID and GC procedures for cities sampled in the 1985 Nineteen Cities Study

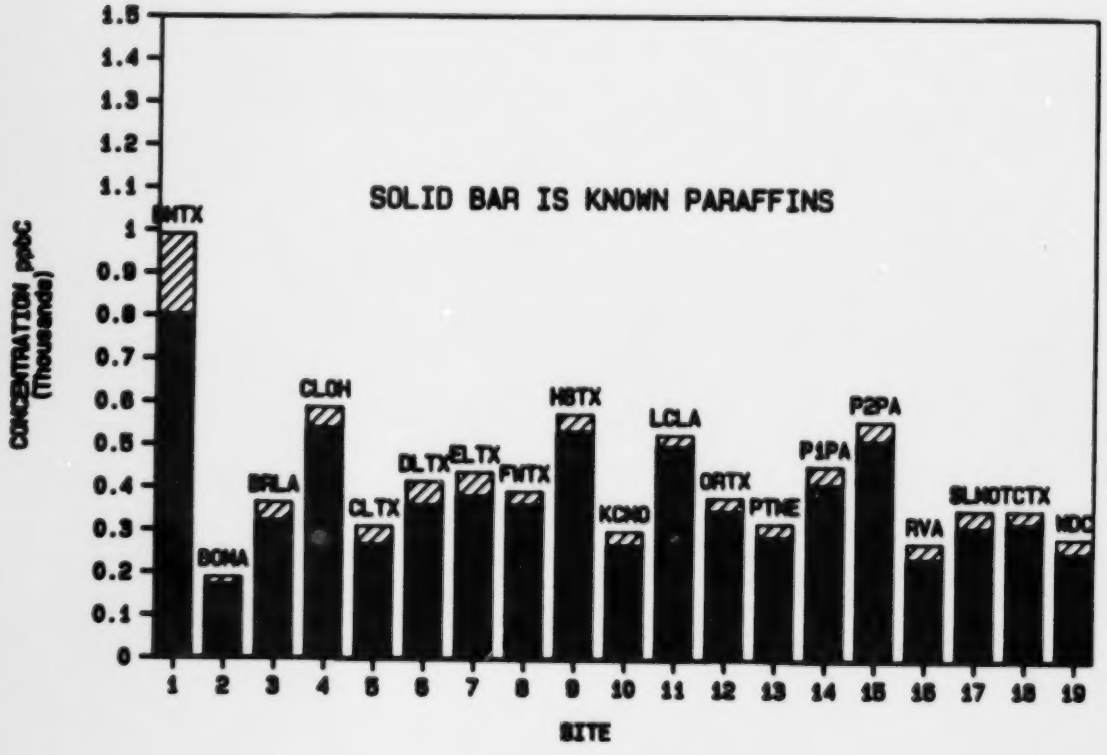


Figure 2. Sum of known and unknown mean paraffin concentrations obtained at the 19 sites in the 1985 study

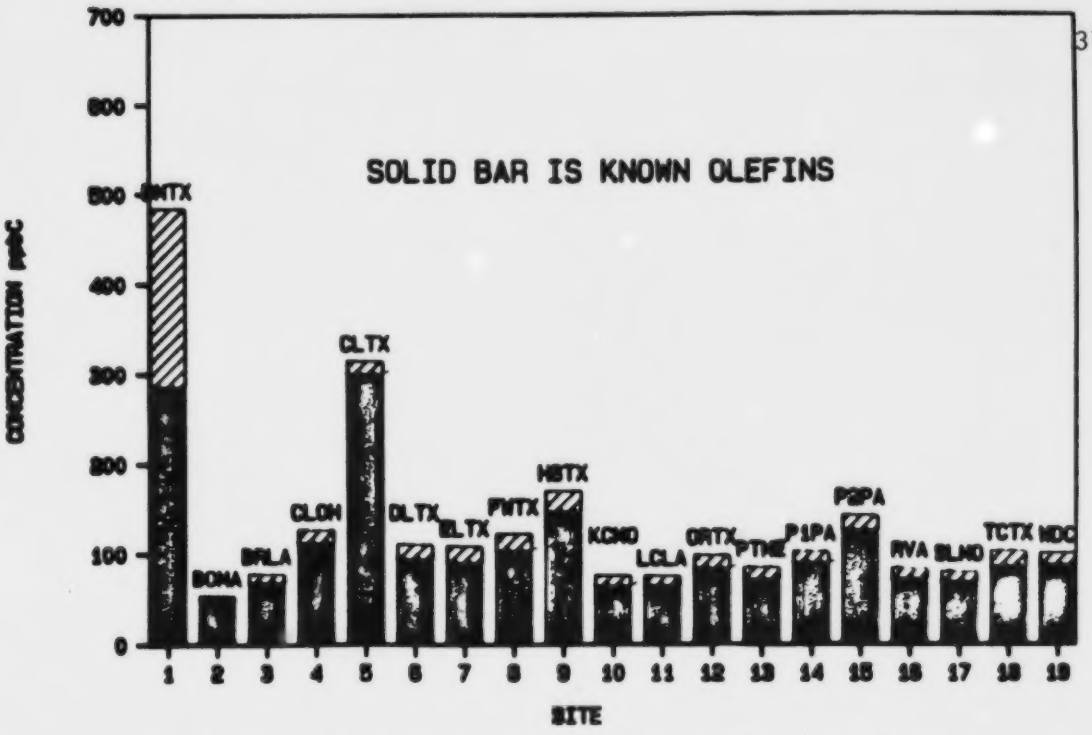


Figure 3. Sum of known and unknown mean olefin concentrations obtained at the 19 sites in the 1985 study

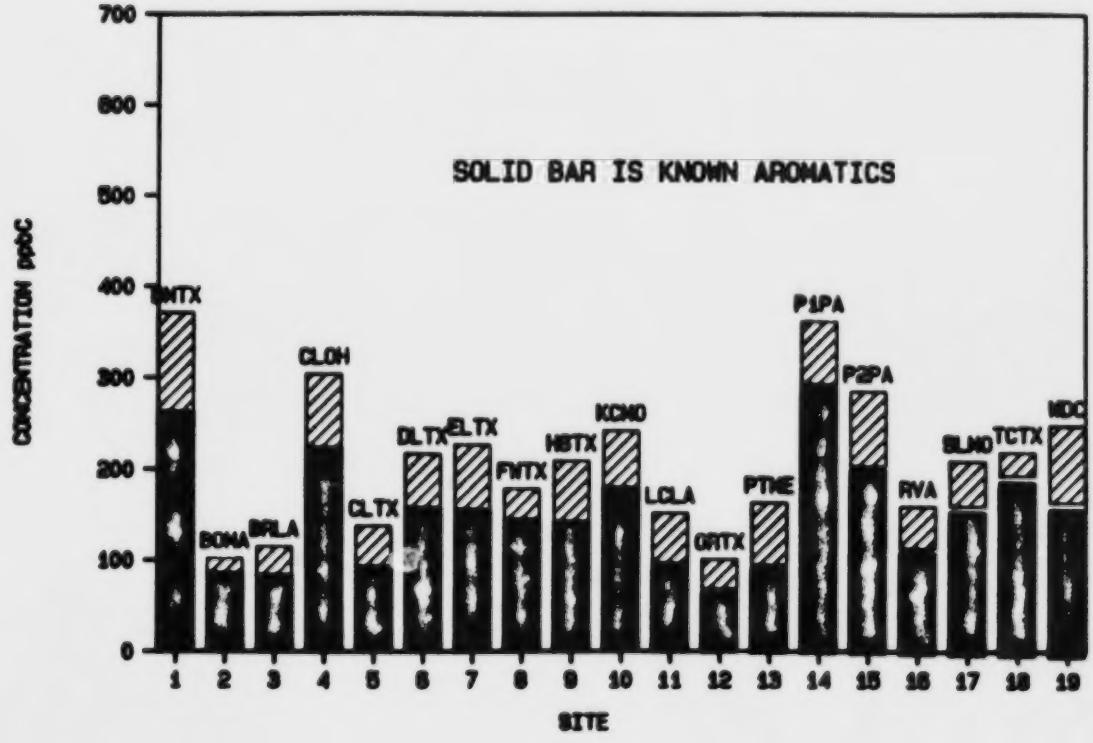


Figure 4. Sum of known and unknown mean aromatic concentrations obtained at the 19 sites in the 1985 study

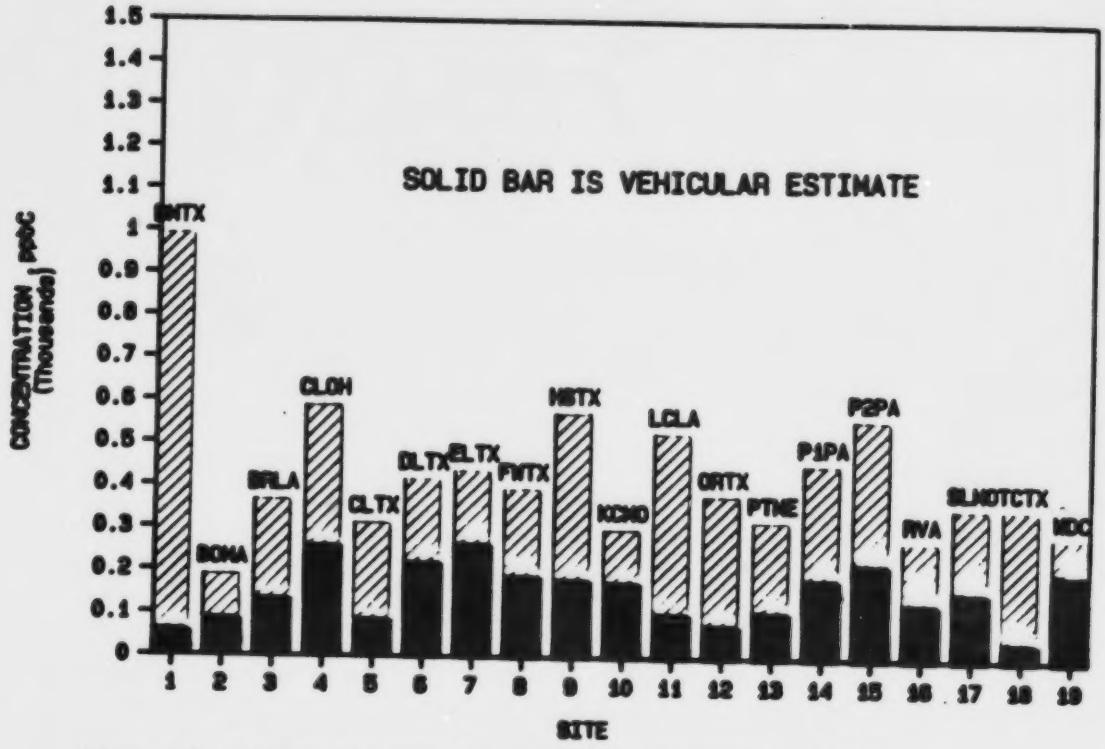


Figure 5. Vehicular and non-vehicular paraffin estimates calculated for the 19 sites in the 1985 study

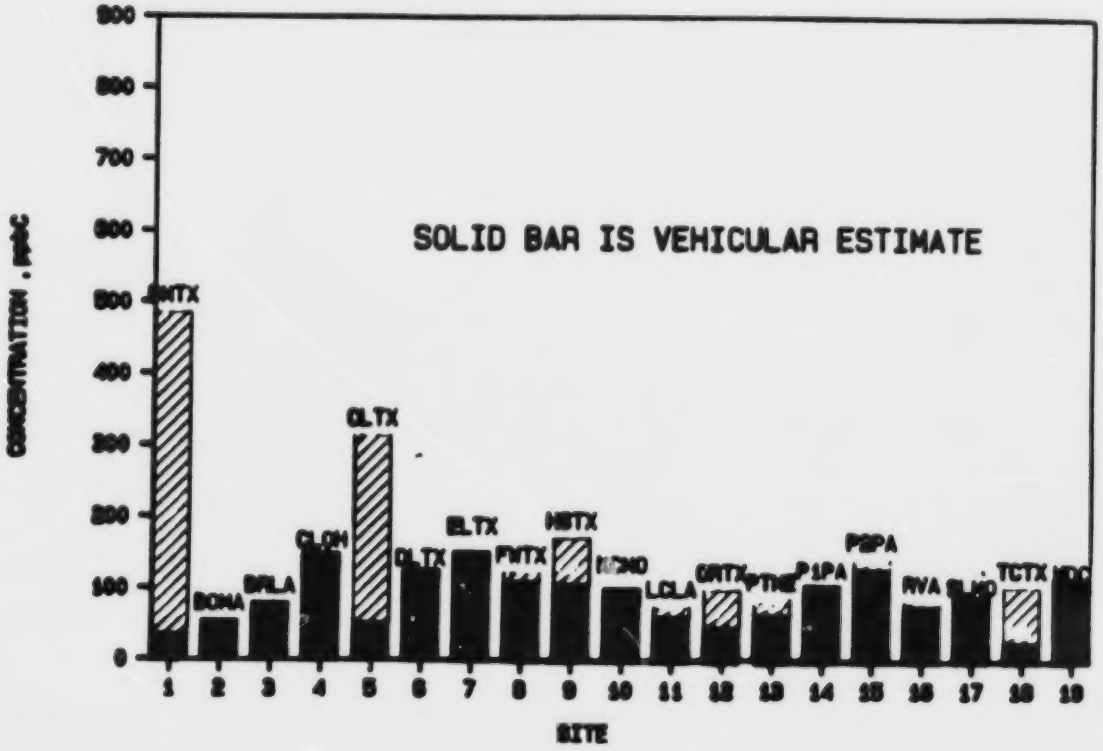


Figure 6. Vehicular and non-vehicular olefin estimates calculated for the 19 sites in the 1985 study

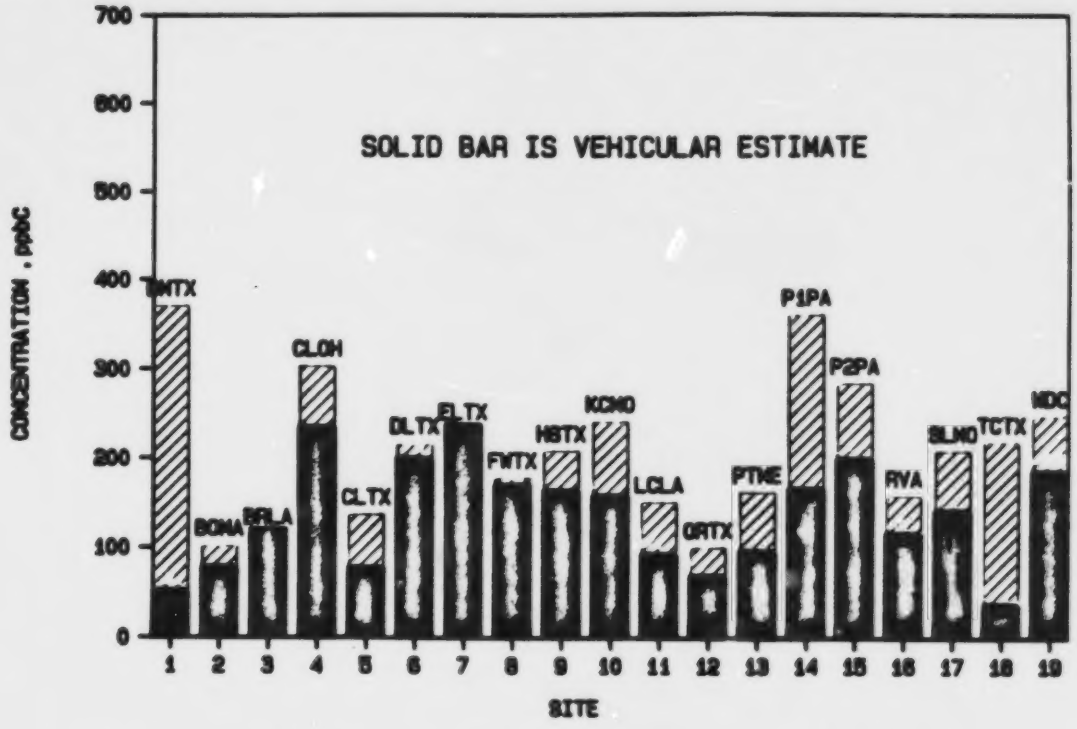


Figure 7. Vehicular and non-vehicular aromatic estimates calculated for the 19 sites in the 1985 study

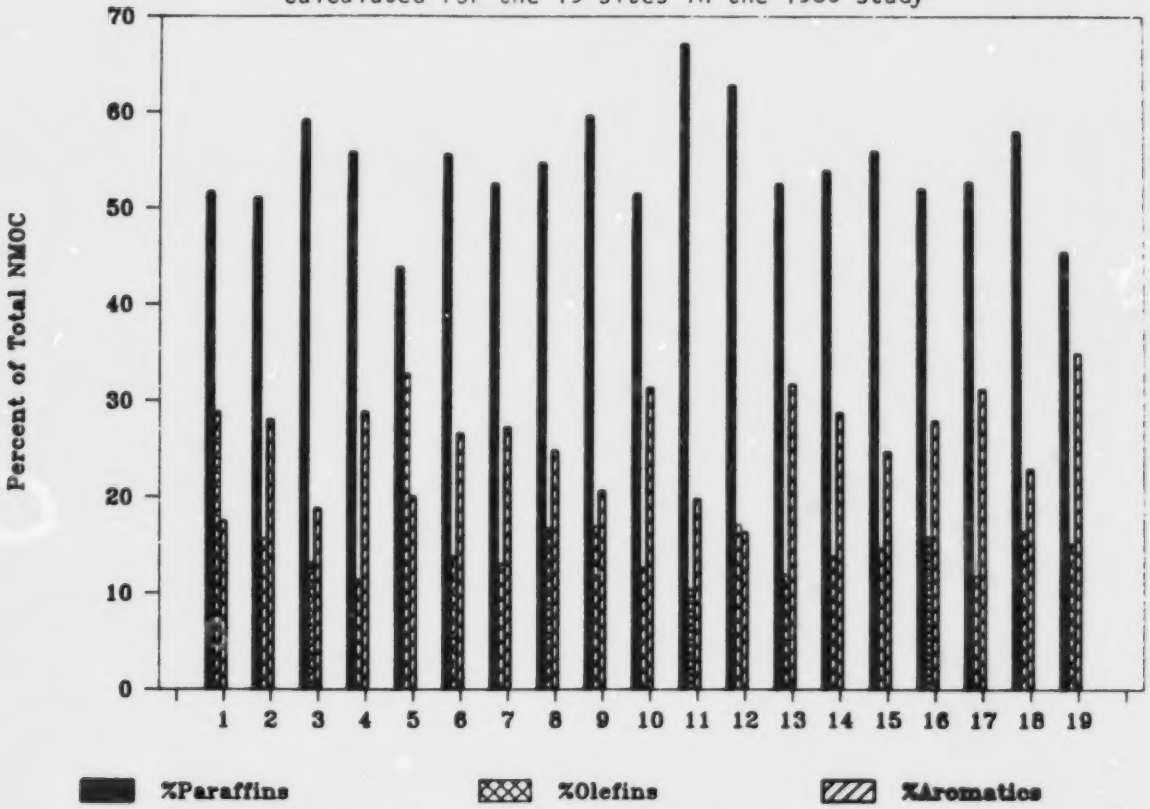


Figure 8. Percentage paraffins, olefins, and aromatics composition for the 19 sites participating in the 1985 study

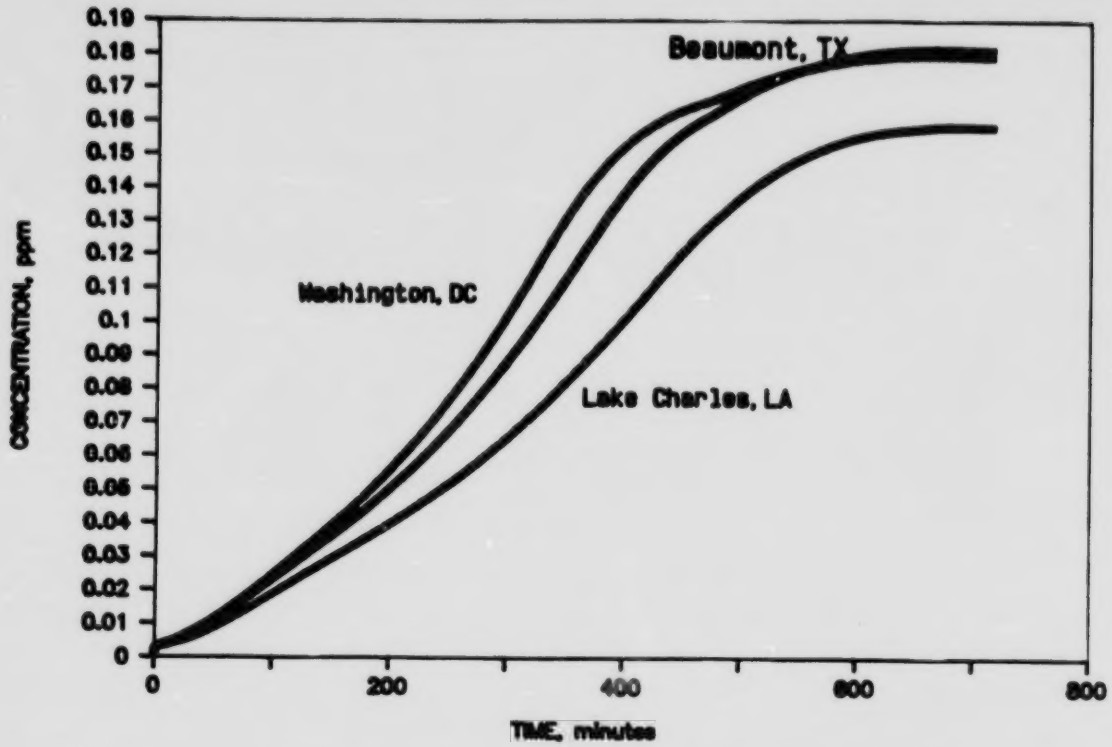


Figure 9. Ozone profiles for 12 hour simulations performed for Beaumont, TX, Washington, DC, and Lake Charles, LA using an NMOC to $NO_x$ ratio of 6

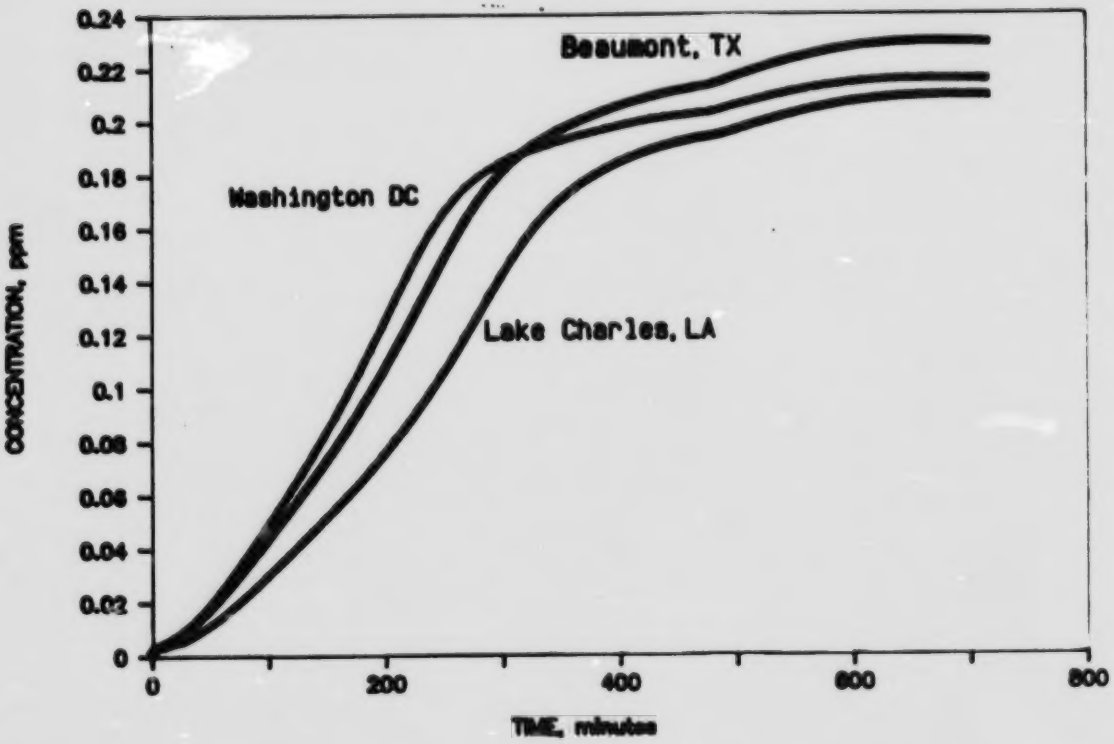


Figure 10. Ozone profiles for 12 hour simulation performed for Beaumont, TX, Washington, DC, and Lake Charles, LA using an NMOC to $NO_x$ ratio of 12

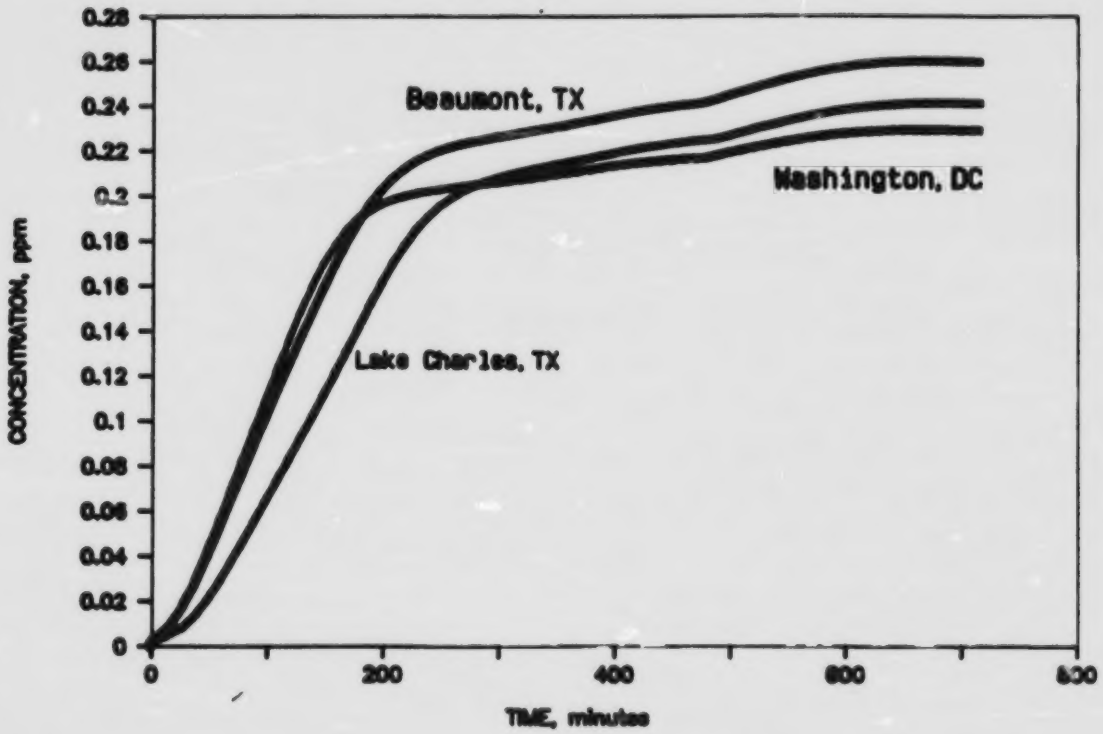


Figure 11. Ozone profile for 12 hour simulations performed for Beaumont, TX, Washington, DC, and Lake Charles, LA using an NMOC to $NO_x$ ratio of 24

# AN EXAMINATION OF OZONE LEVELS IN SELECTED FORESTED AREAS OF THE EASTERN UNITED STATES

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## RÉSUMÉ

Dans le présent exposé, les auteurs analysent les données recueillies sur l'ozone ambiant pendant une période de six ans, 1978 à 1983, dans des stations situées dans les milieux forestiers de l'est des États-Unis. Les paramètres retenus pour caractériser les conditions d'exposition à l'ozone dans ces milieux sont la moyenne de sept heures durant la saison de croissance et le nombre d'heures, durant cette saison, où les concentrations horaires moyennes en ozone sont à ou au-dessus de 0,07, 0,08, 0,10 et 0,12 ppm. L'analyse révèle que les expositions sont les plus faibles en ozone dans les régions le long de la frontière entre le Canada et le nord de la Nouvelle-Angleterre et le nord des Grands Lacs et que ces taux sont au plus haut dans les forêts de pins du New Jersey et dans les basses-terres du Sud.

# AN EXAMINATION OF OZONE LEVELS IN SELECTED FORESTED AREAS OF THE EASTERN UNITED STATES

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## ABSTRACT

Ambient ozone monitoring data from stations located in selected forested areas of the eastern United States were analyzed for the 6-year period 1978 through 1983. Parameters used to characterize the ozone exposure conditions in these forested areas were the 7-hr growing season mean and the number of hours during the growing season with hourly mean ozone concentrations at or above 0.07, 0.08, 0.10, and 0.12 ppm. The analysis revealed lowest ozone exposures in areas along the Canadian border in northern New England and in the upper Great Lakes, and highest exposures in the New Jersey pinelands and southern piedmont.

## INTRODUCTION

The possibility that forest health may be adversely affected by airborne pollutants is a subject of considerable interest in Europe and North America. While evidence of regional scale impacts is presently lacking, results of controlled exposure studies and observations of forest damage near major point sources and in some urbanized areas suggest that regional scale investigations are in order. At present, it appears ozone should be given the highest priority because ambient levels in many parts

of the country are in the range which has been found to elicit visible damage or growth reductions in some plant species (U.S. EPA, 1986).

The purpose of this paper is to examine ambient ozone concentrations in various forested regions in the eastern United States by analyzing readily available ambient monitoring data. A number of exposure parameters have been used to characterize the average exposure conditions over selected forested areas.

## METHODS AND DATA USED

Hourly mean $O_3$ monitoring data for the years 1978 through 1983 were obtained from the (1) United States Environmental Protection Agency Storage and Retrieval of Aerometric Data (SAROAD) data base, (2) Electric Power Research Institute (SURE and ERAQS), (3) Tennessee Valley Authority, and (4) National Park Service. A given site had to monitor for at least one year with at least a 50% data capture rate for the April through October period to be included in the analysis. Only data for the April through October were analyzed; this period is often referred to as the growing season.

For the April through October period, the hourly averaged $O_3$ concentrations were characterized as follows: (1) data capture rate; (2) average concentration between 0900 and 1559 (which will be refered to as the growing season 7-h mean); and (3) number of hours with concentrations equal to or greater than 0.07, 0.08, 0.10, and 0.12 ppm.

Many of the monitoring sites used in the study recorded data over a multiple-year period. In this analysis, multiple-years of data at a site were treated independently. Thus, if the same monitoring site had 3 years of data reported, there were 3

sets of data used in the analysis and this total has been referred to as 3 site-years of data.

Ozone data were characterized for selected forested regions representative of several of the major commercial forest types in the eastern United States. The five geographic areas and associated major forest types examined were (1) upper Great Lakes (mixed northern hardwoods and pine), (2) northern New England and New York (spruce-fir and maple-beech-birch), (3) mid-Atlantic (maple-beech-birch and oak-hickory), (4) New Jersey pinelands (pine and oak), and (5) southeastern/southern (yellow pine). Within the yellow pine region, two areas were examined: the coastal plain area extending from Virginia south and west to eastern Texas and the piedmont/mountain/ridge and valley area encompassing parts of Virginia, North Carolina, South Carolina, Georgia, Alabama, and Tennessee.

The approximate boundaries of these regions are shown in Figure 1. Major metropolitan areas located at the edge of the forested regions were not included since $O_3$ concentrations in these heavily urbanized areas might not be representative of the majority of the forested area where population densities were considerably lower. Otherwise, data from all sites within each of the areas were included. Most of the stations were located in or near population centers, although there were a fair number of rural locations. Sites used in the analysis are indicated in Figure 1.

After characterizing each site-year of data, the calculated parameters for all sites within each of the regions were combined to examine annual average regional distributions of these exposure parameters for each of the 6 years. In addition, all 6 years of data were combined for each region to determine

(1) the magnitude of year-to-year variability relative to the 6 yr mean in each of the regions, and (2) if there were significant differences among regions over the longer term period.

RESULTS

Table I provides a summary of the $O_3$ monitoring data by region, by year, and for the 6-year average for all years combined. The regions have been designated as (1) northern New England/New York, (2) Central New York, Pennsylvania, and Maryland, (3) upper Great Lakes, (4) New Jersey pinelands, (5) piedmont/mountain/ridge and valley, and (6) southern coastal plain. Whiteface Mountain data have been treated separately from other data in the northern New England and New York region because the monitor is situated at the top of Whiteface Mountain (elevation 1485 m), while the remainder of the sites in this region are at low elevations.

An examination of Table I shows that, for the parameters considered in this analysis, ozone concentrations averaged over the entire 6-year period were lowest in the northern New England/New York and upper Great Lakes regions. Concentrations were somewhat higher in the New York/Pennsylvania/Maryland area, considerably higher in the South Coastal Plain and piedmont/mountain/ridge and valley area, and greatest in the New Jersey Pinelands.

With respect to Whiteface Mountain, it can be seen that the distribution of hourly mean concentrations was significantly different from the remainder of the northern New England/New York area. Whiteface had a higher average growing season mean and a greater number of hours with concentrations at or above the various thresholds. It is suspected ozone levels at the Whiteface

site are strongly influenced by transported ozone with only minimal scavenging from local nitric oxide sources and minimal deposition to surfaces such as vegetation. The fact that diurnal variations at Whiteface are minimal, as reported by Lefohn and Mohnen (1986), tends to support this hypothesis.

Table I includes the statistics for each of the 6 years examined. There is considerable variability among years. Factors contributing to this variability obviously include meteorological conditions and differences in the emissions of ozone precursors. The number and location of stations within each of the areas also varied among years. If all regions are considered together, $O_3$ concentrations in 1978, 1980, and 1983 were greater than those in 1979, 1981, and 1982. However, this overall pattern did not necessarily hold for each individual area.

The regional summary statistics in Table I should not be interpreted as representing uniform ozone concentrations across an entire region, but rather as approximate estimates of area-wide mean values. Except for the New Jersey pinelands, the forested regions outlined in Figure 1 cover large areas. Ozone concentrations are not homogenous across the areas because of mesoscale meteorological variations and non-uniform distributions of emission sources.

In the northern New England/New York region, there were no monitoring sites in a large portion of Maine which has a low population density and is primarily commercial forest land. An examination of available data indicated that concentrations generally decreased moving northward away from the populated areas in southern and coastal New England and southeastern New York. The lowest ozone levels occurred at the northernmost sites in Vermont, New Hampshire, and Maine. Highest levels were observed

in the upper Hudson valley and along the southwestern Maine coast. In interior Maine, ozone levels were thus probably on the same order as those seen at the northernmost sites since there are no large population centers in the area.

Most of the monitoring sites in the New York/Pennsylvania/Maryland region were urban oriented, sited either in or downwind of cities. There were no monitors in the large commercial forest region of north central Pennsylvania and adjacent New York. There did not appear to be any consistent pattern of ozone concentrations across the region, with large numbers of occurrences of elevated ozone concentrations seen in different years at different sites. One might speculate that ozone levels in the main forested area of the region are similar to those at the monitoring sites, but actual monitoring data are needed to confirm this conclusion.

Monitoring sites in the upper Great Lakes had an uneven spatial distribution with only one site in the Upper Peninsula, one site in northeastern Minnesota, and one site at the southern edge of the forested area of lower Michigan. Northern Wisconsin had fairly good coverage, but some sites had only one year of usable data. The northernmost sites had very low ozone levels compared to the regional averages. For example, Lake County in northern Minnesota averaged 43 h per year of concentrations at or above 0.07 ppm compared to the regional average of 121 h per year. At the other extreme, Muskegon, MI on the western shore of Lake Michigan had an average of 235 hr per year of ozone concentrations at or above 0.07 ppm. Muskegon is relatively close to large population centers on the shorelines of southern Lake Michigan and is undoubtedly influenced by transported ozone and ozone precursors from these areas. Sites in Wisconsin had ozone

concentrations intermediate to these two extremes.

The two areas covering most of the southern United States are extremely large. There are major population centers such as Richmond, Charlotte, Atlanta, and New Orleans scattered throughout. As Figure 1 shows, monitoring sites were concentrated around urbanized areas, although a number of sites were in rural areas. Georgia, Mississippi, and Arkansas, states with major acreage of commercial forest, had few monitoring sites, all being urban oriented. Pinkerton and Lefohn (1986) analyzed 1983 ozone monitoring data from this region by examining sites located in and adjacent to urbanized areas with populations over 300,000 versus rural sites located more than 50 km from any city with a population over 50,000. They found $O_3$ concentrations were higher in the larger urban areas than elsewhere, but that $O_3$ concentrations in smaller urban areas often were similar to those at rural sites. The number of occurrences of concentrations at or above 0.10 ppm were relatively low in the smaller metropolitan areas and rural areas, but were quite high at one or more monitoring sites in the largest metropolitan areas such as Atlanta.

Within the piedmont/mountain/ridge and valley area, highest ozone concentrations were observed at monitoring sites near Birmingham, Atlanta, Charlotte, and Richmond. Lower values were seen in smaller cities and rural areas. Although the density of monitoring stations was insufficient to develop a detailed spatial distribution of ozone throughout this area, forests adjacent to the larger metropolitan areas were likely exposed to somewhat higher concentrations than forests further away from the larger urban centers.

Monitoring sites in the southern coastal plain were

located primarily in coastal urbanized areas such as Norfolk, Charleston, Jacksonville, Pensacola, Mobile, New Orleans, Baton Rogue, and Beaumont/Port Arthur. As Table I shows, coastal plain ozone concentrations were lower than those in the piedmont/mountain/ridge and valley subregion. Among coastal plain monitoring sites, those in the Norfolk area and in east Texas recorded the greatest frequencies of elevated $O_3$ concentrations by a wide margin. Both of these areas are highly industrialized and densely populated. In addition, monitoring sites in Beaumont/Port Arthur occasionally are influenced by ozone and its precursors transported from the Houston area. With the exception of some of the monitoring sites in the Baton Rogue and New Orleans areas, remaining monitoring sites in the coastal plain both in rural and urban areas experienced quite low ozone concentrations. Although there were significant monitoring voids in the coastal plain in Georgia and Mississippi, it seems reasonable to conclude that ozone exposure conditions in commercial forests in the coastal plain away from the three largest urban areas were somewhat lower than the averages shown in Table I for the coastal plain.

## CONCLUSIONS

The number of occurrences of hourly averaged ozone concentrations at and above the selected values of 0.07, 0.08, 0.10, and 0.12 ppm and the 7 h growing season mean were used to characterize ozone exposure conditions of various forested regions of the eastern United States. Six years (1978-1983) of monitoring data from sites located within each of six forest regions were examined.

Based on this analysis, the following conclusions can be

drawn:

1. Ozone exposures are lowest in the northern New England/New York and upper Great Lakes regions, are higher in the New York/Pennsylvania/Maryland region, are still higher in the southeastern/southern region, and greatest in the New Jersey pinelands. In the southern United States, concentrations are higher in the piedmont/mountain/ridge and valley region than in the coastal plain;
2. There is considerable year-to-year variation in regionwide ozone exposure conditions. In general, higher ozone concentrations were observed in 1978, 1980 and 1983 as compared to the other three years examined;
3. Within regions, there was considerable variability in ozone concentrations. In the northernmost two regions, concentrations were higher in the southern parts of the region. In the south, concentrations were higher around the larger metropolitan areas.

ACKNOWLEDGEMENTS

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Pinkerton, J.E., and Lefohn, A.S. (1986). "Characterization of

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U.S. EPA (1986). Air Quality Criteria for Ozone and Other Photochemical Oxidants, Vol. III. EPA-600/8-84/020cF, Environmental Criteria and Assessment Office, Research Triangle Park, NC 27711.

Table 1. Summary of ozone monitoring data for the period 1978-1983 by area.

| Years | Parameter[2] | Regions[1] NNE/NY | WFM | NY/PA/MD | UGL | NJP | P/M/RV | SCP |
|---|---|---|---|---|---|---|---|---|
| 1978-1983 (Average) | #Site-Yrs | 43 | 6 | 78 | 42 | 17 | 197 | 153 |
| | 7-h | 36 | 43 | 39 | 37 | 53 | 51 | 43 |
| | $n_{70}$ | 103 | 455 | 223 | 121 | 500 | 328 | 205 |
| | $n_{80}$ | 49 | 214 | 116 | 59 | 289 | 162 | 97 |
| | $n_{100}$ | 9 | 29 | 25 | 11 | 90 | 30 | 22 |
| | $n_{120}$ | 1 | 2 | 5 | 3 | 22 | 7 | 6 |
| 1978 | #Site-Yrs | 2 | 1 | 10 | 5 | 1 | 18 | 14 |
| | 7-h | 30 | 49 | 40 | 38 | 44 | 54 | 47 |
| | $n_{70}$ | 67 | 742 | 272 | 160 | 418 | 529 | 362 |
| | $n_{80}$ | 36 | 328 | 159 | 83 | 243 | 326 | 218 |
| | $n_{100}$ | 7 | 36 | 39 | 23 | 86 | 100 | 71 |
| | $n_{120}$ | 2 | 0 | 10 | 8 | 24 | 31 | 21 |
| 1979 | #Site-Yrs | 7 | 1 | 12 | 6 | 3 | 24 | 20 |
| | 7-h | 38 | 49 | 39 | 36 | 50 | 44 | 40 |
| | $n_{70}$ | 133 | 710 | 252 | 112 | 352 | 234 | 144 |
| | $n_{80}$ | 74 | 380 | 133 | 55 | 205 | 118 | 57 |
| | $n_{100}$ | 15 | 59 | 29 | 7 | 68 | 19 | 7 |
| | $n_{120}$ | 1 | 11 | 5 | 1 | 13 | 5 | 1 |
| 1980 | #Site-Yrs | 7 | 1 | 10 | 6 | 4 | 28 | 19 |
| | 7-h | 36 | 46 | 42 | 38 | 55 | 52 | 46 |
| | $n_{70}$ | 121 | 565 | 300 | 179 | 535 | 415 | 315 |
| | $n_{80}$ | 60 | 299 | 176 | 101 | 305 | 205 | 150 |
| | $n_{100}$ | 8 | 48 | 48 | 20 | 80 | 34 | 36 |
| | $n_{120}$ | 1 | 1 | 12 | 2 | 14 | 6 | 13 |
| 1981 | #Site-Yrs | 10 | 1 | 15 | 9 | 3 | 36 | 29 |
| | 7-h | 34 | 39 | 36 | 37 | 54 | 49 | 44 |
| | $n_{70}$ | 44 | 212 | 156 | 65 | 570 | 262 | 194 |
| | $n_{80}$ | 14 | 85 | 67 | 27 | 332 | 121 | 85 |
| | $n_{100}$ | 3 | 3 | 11 | 3 | 104 | 20 | 18 |
| | $n_{120}$ | 0 | 0 | 1 | 1 | 28 | 3 | 4 |
| 1982 | #Site-Yrs | 8 | 1 | 16 | 9 | 3 | 46 | 30 |
| | 7-h | 39 | 37 | 39 | 35 | 53 | 47 | 41 |
| | $n_{70}$ | 104 | 188 | 176 | 70 | 449 | 221 | 164 |
| | $n_{80}$ | 48 | 88 | 82 | 28 | 224 | 92 | 75 |
| | $n_{100}$ | 7 | 17 | 16 | 3 | 47 | 11 | 16 |
| | $n_{120}$ | 0 | 0 | 2 | 1 | 6 | 1 | 5 |
| 1983 | #Site-Yrs | 9 | 1 | 15 | 7 | 3 | 45 | 41 |
| | 7-h | 38 | 39 | 41 | 43 | 55 | 52 | 42 |
| | $n_{70}$ | 139 | 310 | 231 | 190 | 608 | 407 | 168 |
| | $n_{80}$ | 65 | 102 | 119 | 93 | 388 | 197 | 77 |
| | $n_{100}$ | 12 | 10 | 21 | 16 | 158 | 35 | 14 |
| | $n_{120}$ | 2 | 0 | 3 | 5 | 50 | 7 | 2 |

(1) Regions:
- NNE/NY - Northern New England/New York
- WFM - Whiteface Mountain
- NY/PA/MD - Western New York/Central Pennsylvania/Western Maryland
- UGL - Upper Great Lakes
- NJP - New Jersey Pinelands
- P/M/RV - Piedmont/Mountain/Ridge-Valley
- SCP - Southern Coastal Plain

(2) Parameters:
- 7-h - April-October mean of the 0900-1559h daily mean in units of ppb.
- $n_{70}$ - Number of hourly occurrences $\geq$ 0.07 ppm.
- $n_{80}$ - Number of hourly occurrences $\geq$ 0.08 ppm.
- $n_{100}$ - Number of hourly occurrences $\geq$ 0.10 ppm.
- $n_{120}$ - Number of hourly occurrences $\geq$ 0.12 ppm.

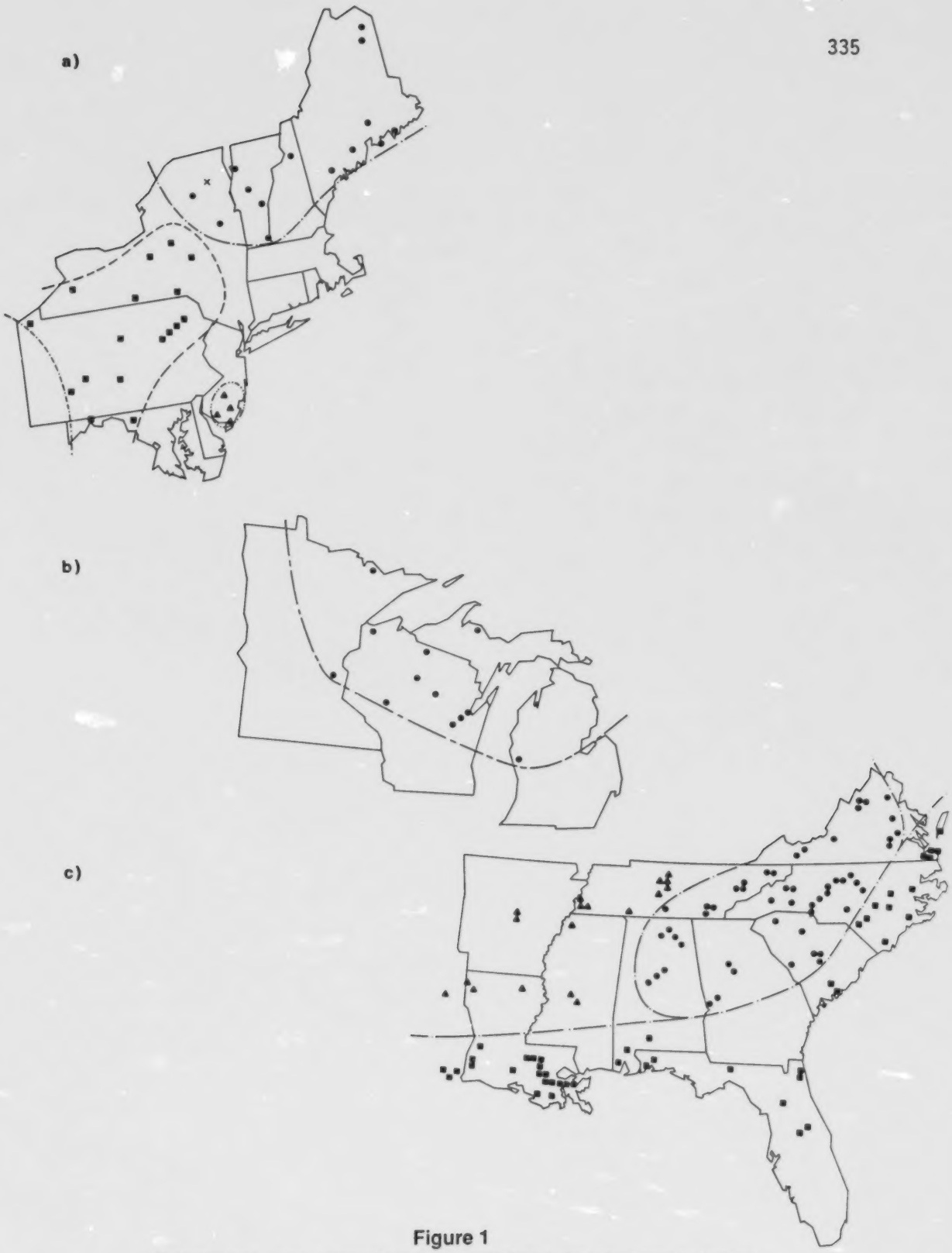


**Figure 1**

Monitoring sites used to characterize ozone concentrations in the a) Northeast: (●) Northern New England/New York, (x) Whiteface Mountain, (■) Central New York/ Pennsylvania/ Maryland, (▲) Pinelands; b) Upper Great Lakes; c) South: (●) Piedmont/Mountain/Ridge and Valley, (■) Coastal Plains, (▲) other.

# NATIONAL AND REGIONAL TRENDS IN AMBIENT OZONE AND NITROGEN DIOXIDE MEASUREMENTS, 1976-1985

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## RÉSUMÉ

Les tendances nationales à long terme sur une période de dix ans (1976 à la fin 1985) et de cinq ans (1981 à la fin 1985) sont examinées pour l'ozone ($O_3$) et le dioxyde d'azote ($NO_2$). À celles-ci s'ajoutent les tendances régionales pour la période de 1983 jusqu'à la fin 1985. Ces données utilisées dans la présente étude proviennent de la Banque nationale de données aérométriques de l'Agence américaine pour la protection de l'environnement (EPA). Toutes les analyses de tendance sur la qualité de l'air ambiant sont basées sur les stations de surveillance qui ont enregistré au moins huit années de données sur dix durant la période 1976 à 1985, ou quatre années sur cinq durant la période 1981 à 1985. Pour chacune des années, un critère d'exhaustivité des données devait être respecté. À l'échelle nationale, la moyenne composée de la deuxième plus forte valeur quotidienne d'$O_3$ pour une heure relevée à 183 sites a diminué de 19 pour cent entre 1976 et 1985. Les émissions de composés organiques volatils (COV) ont décru de onze pour cent au cours de la même période. Bien que la moyenne composée de 1985 est inférieure de 19 pour cent à celle de 1976, l'interprétation de cette dimunition est compliquée par les changements dans la calibration des mesures de l'ozone effectués de 1978 à 1979. Dans la période suivant ces changements, c'est-à-dire 1979 à 1985, les niveaux d'$O_3$ ont diminué de dix pour cent et les émissions de COV de douze pour cent. On estime que le nombre de fois que l'ozone a dépassé la norme a chuté de 38 pour cent entre 1979 et 1985. Les tendances pour l'$O_3$ dans les années 1980 montrent que les valeurs de 1980 et 1983 sont plus élevées que celles de 1981, 1982, 1984 et 1985.

Les taux de dioxyde d'azote ont augmenté de 1976 à 1979 puis ont diminué jusqu'en 1985, exception faite d'un léger accroissement en 1984. Cependant, la moyenne composée du $NO_2$ en 1985 est inférieure de onze pour cent aux taux de 1976. La tendance dans les émissions estimées d'oxydes d'azote à la grandeur du pays suit une courbe semblable à la présence du $NO_2$ dans l'air. Entre 1976 et 1985, les émissions totales d'oxydes d'azote ont diminué d'un pour cent, mais les émissions provenant des automobiles, appartenant à la catégorie ayant sans doute le plus d'incidence sur la majorité des sites de surveillance du $NO_2$, ont décru de quatre pour cent.

Le présent exposé examine les tendances régionales et traite aussi des tendances sur une période de cinq ans. L'ozone continue d'être un problème à grande portée. Plus de 76 millions de personnes vivent dans des milieux où les normes sur l'ozone sont transgressées. Dans le cas du $NO_2$, la norme n'est violée que dans une grande région métropolitaine, celle de Long Beach près de Los Angeles en Californie.

## ABSTRACT

Long-term 10-year (1976 through 1985) and 5-year (1981 through 1985) national trends are examined for ozone ($O_3$) and nitrogen dioxide ($NO_2$). The national trends are complemented with regional trends for the period 1983 through 1985. The data used in this paper came from the U.S. Environmental Protection Agency's National Aerometric Data Bank (NADB). All of the ambient air quality trend analyses are based on monitoring sites which recorded at least 8 of the 10 years of data in the period 1976 to 1985 or 4 out of 5 years in the period 1981 to 1985. An annual data completeness criterion had to be satisfied in each year. Nationally, the composite average of the second highest daily maximum 1-hour $O_3$ values, recorded at 183 sites, decreased 19 percent between 1976 and 1985. Volatile organic compound (VOC) emissions decreased 11 percent during the same period. Although the 1985 composite average is 19 percent lower than the 1976 average, the interpretation of this decrease is complicated by a calibration change for ozone measurements that occurred in the 1978-79 time period. In the post calibration period (1979 to 1985), $O_3$ levels decreased 10 percent, while VOC emissions decreased 12 percent. The estimated number of exceedances of the ozone standard decreased 38 percent between 1979 and 1985. The $O_3$ trends in the 1980's show that the 1980 and 1983 values were higher than those in 1981, 1982, 1984, and 1985.

Nitrogen dioxide levels increased from 1976 to 1979, and decreased through 1985, except for a slight increase in 1984. The 1985 composite $NO_2$ average, however, is 11 percent lower than the 1976 level. The trend in the estimated nationwide emissions of nitrogen oxides follows a pattern similar to the $NO_2$ air quality. Between 1976 and 1985, total nitrogen oxide emissions decreased by 1 percent, but highway vehicle emissions, the source category likely impacting the majority of $NO_2$ monitoring sites, decreased by 4 percent.

This paper examines regional trends and focuses on 5-year trends as well. Ozone continues to be an extremely pervasive problem with over 76 million people living in counties which violated the ozone standard, while the $NO_2$ standard is only violated in one major metropolitan area - Los Angeles - Long Beach, California.

## INTRODUCTION

Ozone ($O_3$) is a colorless, highly reactive gas which is the principal component of smog. It is not emitted directly by specific sources. Instead, it is formed in the air by chemical reactions between nitrogen oxides and volatile organic compounds, such as the vapors of gasoline, chemical solvents, and the combustion products of various fuels. Since these reactions are stimulated by sunlight, ozone reaches peak levels in most parts of the country during the summer. It is a pulmonary irritant which decreases the ability of the lungs to function properly, which is particularly critical to asthmatics and chronic brochitics, as well as exercising healthy adults and children.

Nitrogen dioxide ($NO_2$), a yellowish, brown gas, is present in urban atmospheres through emissions from two major sources; transportation and stationary fuel combustion. The major mechanism for the formation of $NO_2$ in the atmosphere is the oxidation of the primary air pollutant, nitric oxide. When inhaled, $NO_2$ causes impairment of the lung function, causes chest discomfort and coughing, and aggravates preexisting pulmonary illnesses. $NO_2$ also appears to reduce the body's resistence to bacterial infection.

This paper focuses on 10-year, 5-year and short-term trends in $O_3$ and $NO_2$. The national air quality trends are presented for all sites and the National Air Monitoring Station (NAMS) sites. The NAMS were established through monitoring regulations promulgated in May 1979 (Federal Register, 1979) to provide accurate and timely data to the U.S. Environmental Protection Agency (EPA) from a national air monitoring network. The NAMS are located in areas with high pollutant concentrations and high population exposure. These stations meet uniform criteria for siting, quality assurance, reference of equivalent analytical methodology, and sampling intervals to assure consistent data reporting among the States. Other sites operated by the State and local air pollution control agencies, such as the State and Local Air Monitoring Stations (SLAMS) and Special Purpose Monitors (SPM), in general also meet the same rigid criteria, except that in addition to being located in the area of highest concentration and high population exposure, they are located in other

areas as well. The ambient levels presented are averages of direct measurements.

In addition to ambient air quality, trends are also presented for annual nationwide emissions. These emissions are estimated using the best available engineering calculations. The emission trends are taken from the EPA publication, National Air Pollutant Emission Estimates, 1940-1985 and the reader is referred to this publication for more detailed information. The emission data are reported as teragrams (one million metric tons) emitted to the atmosphere per year. These are estimates of the amount and kinds of pollution being generated by automobiles, factories, and other sources, based upon the best available engineering calculations for a given time period.

DATA BASE

The ambient $O_3$ and $NO_2$ data were obtained from the U.S. Environmental Protection Agency's (EPA's) National Aerometric Data Bank (NADB). Air quality data are submitted to the NADB by both State and local governments, as well as federal agencies. At the present time there are over 250 million air pollution measurements on the NADB, the vast majority of which represent the more heavily populated urban areas of the nation.

The size of the available air quality trends data base has been expanded by merging data at sites which have experienced changes in the agency operating the site, the instrument used, or a change in the project code, such as a change from population oriented to special purpose monitoring. In order for a monitoring site to have been included in the national 10-year trend analysis, the site had to contain at least 8 out of the 10 years of data in the period 1976 to 1985. For the national 5-year trend, the site had to contain 4 out of 5 years of data to be included as a trend site. Each year with data had to satisfy an annual data completeness criterion. To begin with, the air quality data are divided into two major groupings -- 24-hour measurements and continuous 1-hour measurements. The 24-hour measurements are obtained from monitoring instruments that produce one measurement per 24-hour period and are operated on a systematic sampling schedule of once every 6 days

or 61 samples per year. Such instruments are sometimes used to measure $NO_2$. For these measurement methods, the NADB defines a valid quarter's record as one consisting of at least five sample measurements representatively distributed among the months of that quarter. Distributions of measurements that show no samples in 2 months of a quarter or that show no samples in 1 month and only one sample in another month are judged unacceptable for calculating a representative estimate of the mean. A valid annual mean for $NO_2$, measured with this type of sampler, requires 4 valid quarters to satisfy the NADB criteria.

The 1-hour data are obtained from monitoring instruments that operate continuously, producing a measurement every hour for a possible total of 8760 hourly measurements in a year. For continuous hourly data, a valid annual mean for $NO_2$ requires at least 4380 hourly observations.

All ozone data are 1-hour values obtained from monitoring instruments that operate continuously. Because of the seasonal nature of ozone, both the second daily maximum 1-hour value and the estimated number of exceedances of the $O_3$ NAAQS were calculated for the $O_3$ season, which varies by State (Federal Register, 1986). For example, in California the $O_3$ season is defined as 12 months, January through December, while in New Jersey it is defined as 7 months, April through October. In order for a site to be included, it had to have a least 50 percent of the daily data in the $O_3$ season.

## TREND STATISTICS

The air quality statistics used in these trend analyses relate to the $O_3$ and $NO_2$ National Ambient Air Quality Standards (NAAQSs). The $O_3$ standard requires that the expected number of days per calendar year with daily maximum hourly concentrations exceeding 0.12 parts per million (ppm) be less than or equal to one. The $NO_2$ NAAQS is an annual arithmetic mean concentration of 0.053 ppm which is not to be exceeded.

The air quality trends information is presented using trend lines, confidence intervals, boxplots (Tukey, 1977) and bar graphs. This paper

presents statistical confidence intervals to facilitate a better understanding of measured changes in air quality. Confidence intervals are placed around composite averages, which are based on sites that satisfy annual data completeness requirements. The confidence intervals can be used to make comparisons between years; if the confidence intervals for any 2 years do not overlap, then the composite averages of the 2 years are significantly different (Figure 1). Ninety-five percent confidence intervals for composite averages of annual arithmetic means and second maxima were calculated from a two-way analysis of variance followed by an application of the Tukey Studentized Range (Winer, 1971). The confidence intervals for composite averages of estimated exceedances were calculated by fitting Poisson distributions (Johnson et al., 1969) to the exceedances each year and then applying the Bonferroni multiple comparisons procedure (Miller, 1981). The utilization of the procedures is explained in publications by Pollack, Hunt and Curran (Pollack et al., 1984) and Pollack and Hunt (Pollack et al., 1985).

The boxplots have the advantage of displaying, simultaneously, several features of the data. Figure 2 illustrates the use of this technique in presenting the 5th, 10th, 25th, 50th (median), 75th, 90th, and 95th percentiles of the data, as well as the composite average. The 5th, 10th and 25th percentiles depict the "cleaner" sites. The 75th, 90th and 95th depict the "dirtier" sites, and the median and average describe the "typical" sites. For example, 90 percent of the sites would have concentrations lower than the 90th percentile. Although the average and median both characterize typical behavior, the median has the advantage of not being affected by a few extremely high observations. The use of the boxplots allow us to simultaneously compare trends in the "cleaner", "typical" and "dirtier" sites.

Boxplots of all trend sites are presented for each year in the 10-year trend. In the recent 5-year trend, the boxplots are presented for the years 1981 through 1985. Emphasis is placed on the post-1980 period to take advantage of the larger number of sites and the fact that the data from the post-1980 period should be of the highest quality, with sites meeting uniform siting criteria and high standards of quality assurance.

Bar graphs are used for the Regional comparisons with the 5-year trend data base. The composite average of the appropriate air quality statistic of the years 1983, 1984 and 1985 are presented. The approach is simple and it allows the reader at a glance to compare the short-term trend in all ten EPA Regions (Figure 3).

In addition to the standard related statistics, other statistics are used, when appropriate, to further clarify observed number of exceedances of the short-term NAAQS's. The estimated number of exceedances is the measured number of exceedances adjusted to account for incomplete sampling.

Finally, trends are also presented for annual nationwide emissions. These emissions data are estimated using the best available engineering calculations. The emission data are reported as teragrams (one million metric tons) emitted to the atmosphere per year (National Air Polluant Emission Estimates, 1940-1985). These are estimates of the amount and kinds of pollution being generated by automobiles, factories, and other sources.

OZONE TREND

The trends site selection process resulted in 183 sites being selected for the 1976-85 period and 523 sites qualifying for the 1981-85 5-year data base. Sixty-five of the long-term trends sites were NAMS while 196 NAMS sites were included in the 5-year trends data base. In both cases, the 5-year data base is about three times as large as the 10-year data base which reflects the improvement in ambient ozone monitoring networks.

## Ten-Year Ozone Trends: 1976-85

Figure 4 displays the 10-year composite average trend for the second high day during the ozone season for the 183 trends sites and the subset of 65 NAMS sites. While the 1985 composite average for the 183 trend sites is 19 percent lower than the 1976 average, the interpretation of this decrease is complicated by a calibration change for ozone measurements that occurred in the 1978-79 time period (Federal Register, 1978). The stippled portion of Figure 4 indicates data affected by measurements taken prior to the calibration change. This complication has been discussed in previous reports (National Air Quality and Emissions Trends Report, 1984) (National Air Quality and Emissions Trends Report, 1983). Part of the problem in quantifying exactly how much of the 1978-79 decrease is due to the calibration change is that not all agencies made the change at the same time and for some States the data prior to 1979 already accounted for the calibration change. Therefore, trend comparisons involving data prior to 1979 should be viewed with caution and an awareness of the possible effect of the calibration change. Comparing the 1985 and 1979 levels shows a 10 percent decrease in the composite average for all trend sites and also for the subset of NAMS. An examination of the confidence intervals about the NAMS sites and all sites suggests that the 1985 composite average is significantly less than the 1979, 1980 and 1983 averages, but is not significantly different from the 1981, 1982 and 1984 averages.

The 10-year trend for the annual second highest daily maximum for the 183 site data base is displayed in Figure 5 using the boxplot presentation. Again, the pre-1979 values are affected by the calibration change, but the patterns from 1979 on are reasonably consistent across all percentiles. Perhaps the most obvious feature is that the 1979, 1980 and 1983 levels are similar and higher than those for 1981, 1982, 1984, and 1985. The 1985 levels are lower than those in the other years. Figure 6 presents the 1976-85 trend for the composite average number of ozone exceedances. This statistic is adjusted for missing data and reflects the number of days that the level of the ozone standard is exceeded during the ozone season. The stippled area again indicates the time period when comparisons would be affected by the calibration change so that the 63 percent decrease between 1976 and 1985

incorporates the effect of the calibration change. Between 1979 and 1985 the expected number of exceedances decreased 38 percent for the 183 sites with a 42 percent decrease for the subset of NAMS sites. As with the second maximum, the 1985 values are the lowest with the 1979, 1980 and 1983 values being higher than those for 1981, 1982, 1984 and 1985.

Table 1 and Figure 7 display the 1976-85 emission trends for volatile organic compounds (VOC) which, along with nitrogen oxides, are involved in the atmospheric chemical and physical processes that result in the formation of $O_3$. Total VOC emissions are estimated to have decreased 11 percent between 1976 and 1985 (National Air Pollutant Emission Estimates, 1940-1985). As shown in Table 1, the annual total for each year of the 1980's is less than any of the annual totals for the 1976-79 period. Between 1976 and 1985, VOC emissions from transportation sources are estimated to have decreased 30 percent despite a 26 percent increase in vehicle miles of travel during this same time period. While most of the source categories showed long-term improvement, the fuel combustion component increased. Fuel combustion accounted for 5 percent of the total VOC emissions in 1976 compared to 12 percent in 1985.

## Five-Year Ozone Trends: 1981-85

By restricting the analysis to the 1981-85 time period, it is possible to expand the trends data base to include 523 sites. Figure 8 uses a boxplot presentation of the annual second maximum daily value at these sites. Although the national composite average decreased 5 percent between 1981 and 1985, the more obvious feature of this graph is that 1983 levels were much higher than those of the other four years. Previous reports (National Air Quality and Emissions Trends Report, 1984) (National Air Quality and Emissions Trends Report, 1983) have discussed the likelihood that these higher 1983 levels were influenced by meteorological conditions in that year that were more conductive to ozone formation than conditions in adjacent years. While 1985 levels are similar to 1984, there was a slight improvement of 2 percent in the national composite average between these 2 years.

As shown in Table 1, total VOC emissions are estimated to have decreased by only 1 percent between 1981 and 1985. Transportation sources decreased by 9 percent during this period. Between 1984 and 1985, both total VOC emissions and the transportation component showed a decrease of approximately 2 percent which is similar to the ambient air quality improvement.

Figure 9 presents a regional comparison for 1983, 1984, and 1985 of the composite average second highest daily maximum 1-hour ozone concentration. For nine of the ten EPA Regions, 1983 was the highest of these 3 years. The only exception to this pattern was in Region X, the northwest. The 1985 levels were also lower than those of 1984 for most parts of the country.

## NITROGEN DIOXIDE

The trends site selection process yielded 108 sites for the 1976-85 ten-year period and 243 sites for the 1981-85 5-year data base. Eleven of the long-term trend sites are NAMS while 46 NAMS are included in the 1981-85 data base. The size of the long-term data base has been decreasing each successive year as low concentration sites are discontinued or as "bubbler" instruments measuring 24-hour values of $NO_2$ are replaced with continuous instruments. In this latter case, data from these two different methods are not merged. Only 33 of the 108 long-term trend sites are $NO_2$ bubblers.

### Ten-year $NO_2$ Trends: 1976-85

The composite average long-term trend for the nitrogen dioxide mean concentration at the 108 trend sites, and the 11 NAMS sites, is shown in Figure 10. Nationally, at all sites, annual average $NO_2$ levels increased from 1976 to 1979, and decreased through 1985, except for a slight increase in 1984. The 1985 composite average $NO_2$ level is 11 percent lower than the 1976 level, indicating a downward trend during this period. Of the 108 trends sites, only 11 are designated as NAMS. This to be expected because $NO_2$ does not present a significant air quality problem in most areas at this time.

Also, NAMS for $NO_2$ are only located in urban areas with populations of 1,000,000 or greater. The composite averages of the NAMS, which are located in eight large metropolitan areas, are higher than those of all sites. Comparing 1985 data to the 1976 levels shows an 11 percent decrease in the composite average for all trends sites and a 14 percent decrease for the NAMS. The discrepancy between all the sites and NAMS year to year changes may be attributed to both the small number of NAMS meeting the 10-year trends completeness criteria and the generally low levels of recorded $NO_2$ annual mean concentrations, with respect to the level of the $NO_2$ NAAQS.

In Figure 10, the 95 percent confidence intervals about the composite means allow for comparisons among the years. While there are no significant differences among the years for the NAMS, because there are so few sites meeting the historical trends criteria, there are significant differences among the composite means of the 108 long-term trends sites. Although the 1984 and 1985 composite mean $NO_2$ levels are not significantly different from one another, they are significantly less than the earlier years 1977 through 1980.

Long-term trends in $NO_2$ annual average concentrations are also displayed in Figure 11 with the use of boxplots. The improvement in the composite average between 1979 and 1985 can also be seen in the upper percentiles. The lower percentiles show little change, however.

The trend in the estimated nationwide emissions of nitrogen oxides ($NO_x$) is similar to the $NO_2$ air quality trend. Table 2 shows $NO_x$ emissions increasing from 1976 through 1978 and generally decreasing until 1984. Between 1976 and 1985 total nitrogen oxide emissions decreased by 1 percent, but highway vehicle emissions, the source category likely impacting the majority of urban $NO_2$ sites, decreased by 4 percent. Figure 12 shows that the two primary source categories of nitrogen oxide emissions are fuel combustion and transportation.

## Five-year $NO_2$ Trends: 1981-85

Figure 13 uses the boxplot presentation to display recent trends in nitrogen dioxide annual mean concentrations for the years 1981-85. Focusing on the past 5 years, rather than the last 10 years, more than doubles the number of sites, from 108 to 243, available for the analysis. Although the composite means from the recent period are lower than the lower long-term means, the trends are consistent for the two data bases.

The composite average $NO_2$ level at the 243 trend sites decreased 5 percent between 1981 and 1985. During this same period, nitrogen oxide emissions decreased by 1 percent. Between 1984 and 1985, the $NO_2$ composite average decreased 2 percent, while nitrogen oxide emissions recorded a 2 percent increase. This small year-to-year difference between the ambient and emissions percent change is likely not significant given the relatively low ambient $NO_2$ levels.

Regional trends in the composite average $NO_2$ concentrations for the years 1983-85 are displayed in Figure 14 using bar graphs. As indicated in the figure, Regions I and IX recorded the highest composite averages during the past 3 years. The pattern of the year-to-year changes is mixed among the regions, however, with seven of the ten Regions showing decreases between 1984 and 1985.

## CONCLUSIONS

While there has been improvement in $O_3$ levels over the post $O_3$ calibration period, 1979 to 1985, there has been little change in $O_3$ levels over the last 5 years, 1981 to 1985. This is consistent with what would be expected, given that the estimated change in nationwide VOC emissions over this period is only 1 percent. Of particular importance is the potential impact of meteorology. Ozone levels in 1983 were significantly higher than 1981, 1982, 1984, and 1985. Earlier reports (National Air Quality and Emissions Trends Report, 1984) (National Air Quality and Emissions Trends

Report, 1983) addressed this issue and found that it was likely that 1983 meteorological conditions were more conducive to $O_3$ formation than in the other years. Comparing 1983 and 1985 levels it is interesting to note that 1985 estimated VOC emissions are 2.5 percent higher than the 1983 estimated VOC emissions, while the 1985 composite average $O_3$ level is 11 percent lower than the 1983 level. Clearly, meteorology is a significant factor that should be taken into account in interpreting trends in ambient $O_3$ levels. Further, in estimating sensitivity of $O_3$ levels to VOC and/or $NO_x$ reductions, several meteorological scenarios should be considered.

As in the case of $O_3$, there has been little change in $NO_2$ levels over the last 5 years. Emphasis is placed on the last 5 years, because of the larger number of $NO_2$ trend sites available for analysis, 243 versus 108 for the 10-year period, 1976-85. Further, the 1981-85 data should be of the highest quality meeting the quality assurance requirements of the monitoring regulations (Federal Register, 1979). Between 1981 and 1985, $NO_2$ levels decreased 5 percent, while $NO_x$ emissions decreased 1 percent.

In evaluating the impact of the VOC and $NO_x$ emission control program, it is important to consider the impact of growth. For example, while estimated VOC and $NO_x$ emissions both decreased 1 percent between 1981 and 1985, Americans increased their driving by over 200 billion vehicle miles. In spite of the growth in vehicle miles travelled, VOC and $NO_x$ emissions due to transportation decreased 9 and 4 percent, respectively, over the 1981 to 1985 period. A recent report (National Air Pollutant Emission Estimates, 1940-1985) calculates theoretical 1985 national VOC and $NO_x$ emission estimates of 35.8 and 24.3 million metric tons, respectively, if there had been no change in the degree of control from 1970. These theoretical estimates are 68 and 22 percent higher than their corresponding estimated 1985 actual VOC and $NO_x$ emissions of 21.3 and 20.0 million metric tons.

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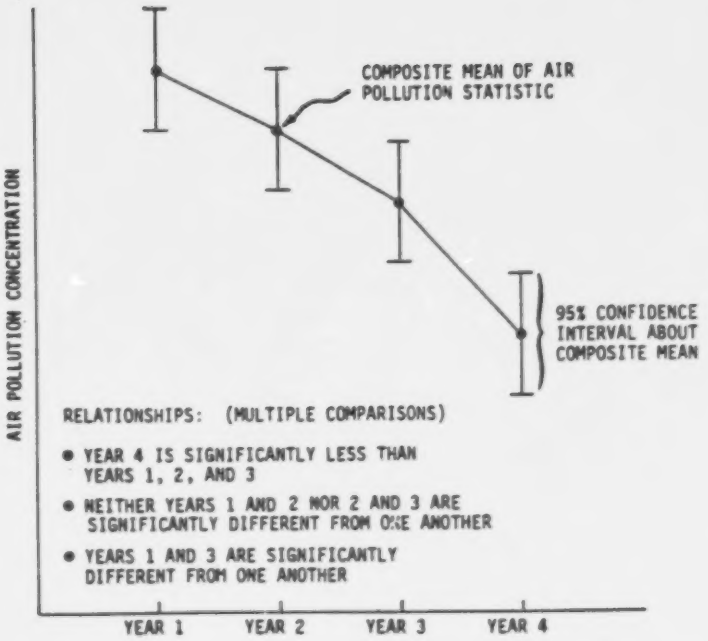


Figure 1. Sample illustration of use of confidence intervals to determine statistically significant change.

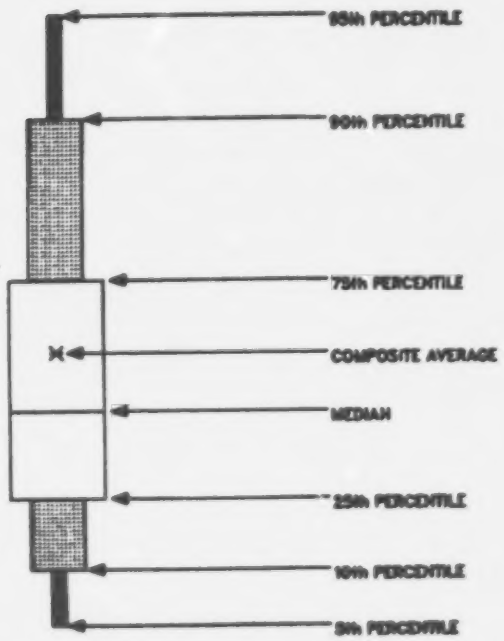


Figure 2. Illustration of plotting conventions for box plots.

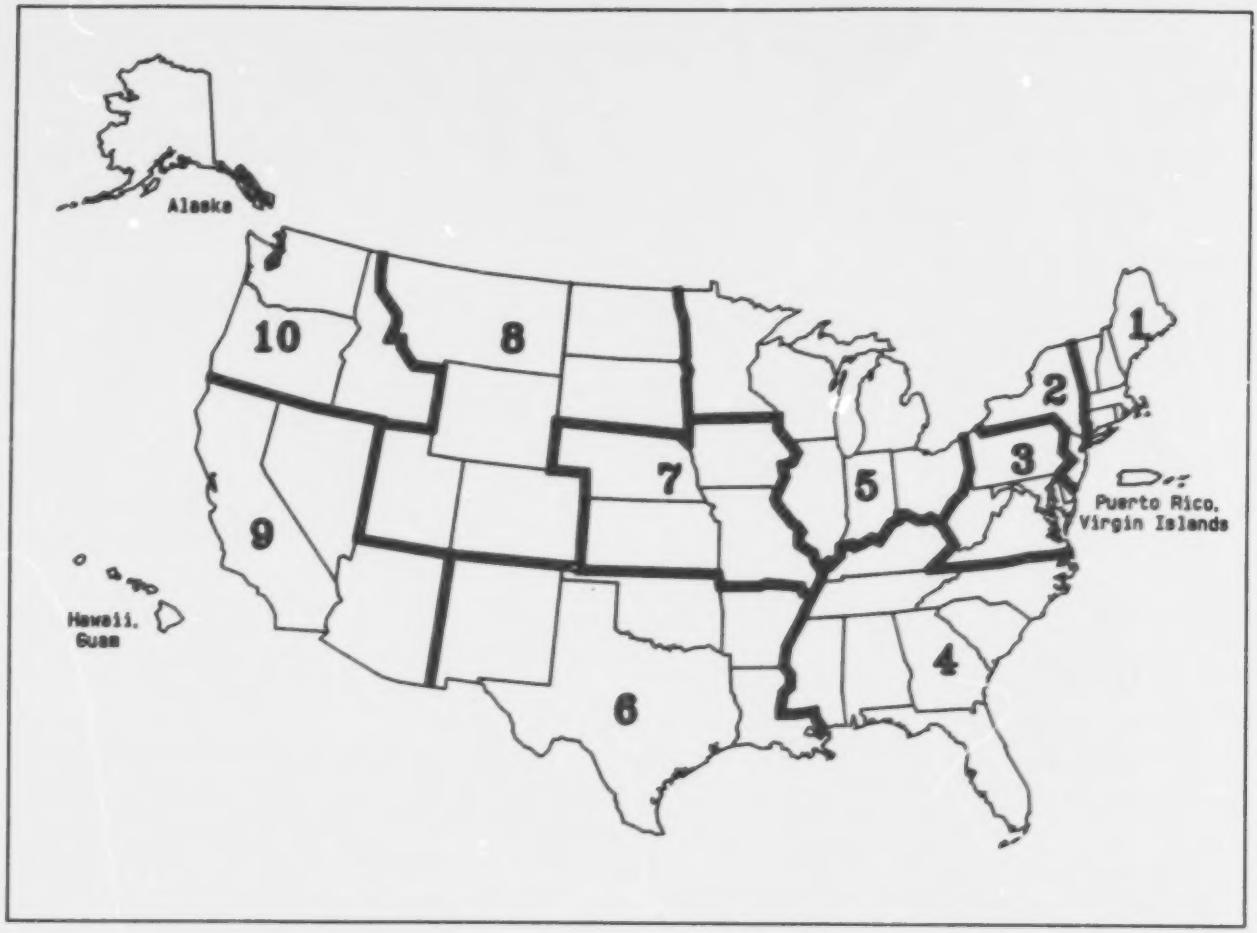


Figure 3. Ten Regions of the U.S. Environmental Protection Agency.

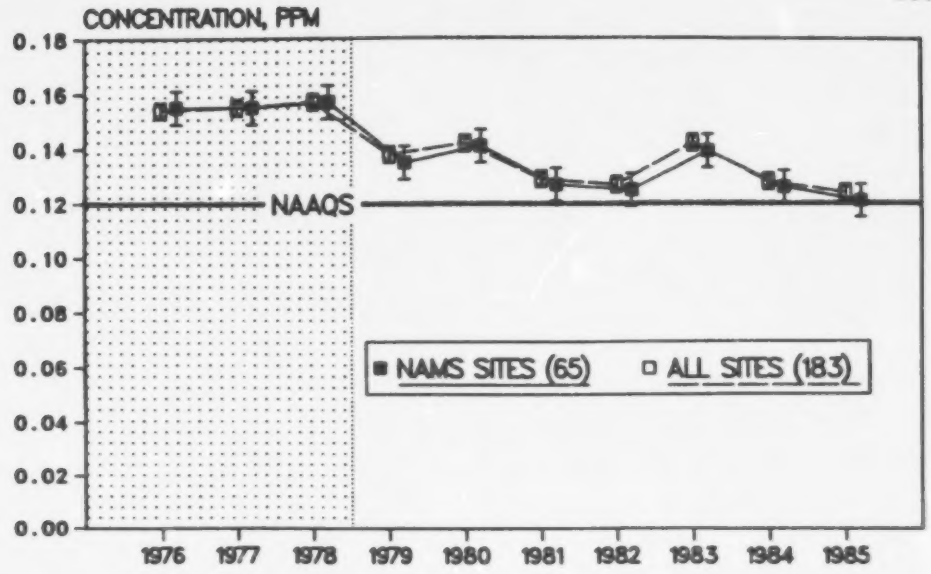


Figure 4. National trend in the composite average of the second highest maximum 1-hour ozone concentration at both NAMS and all sites with 95 percent confidence intervals, 1976-1985.

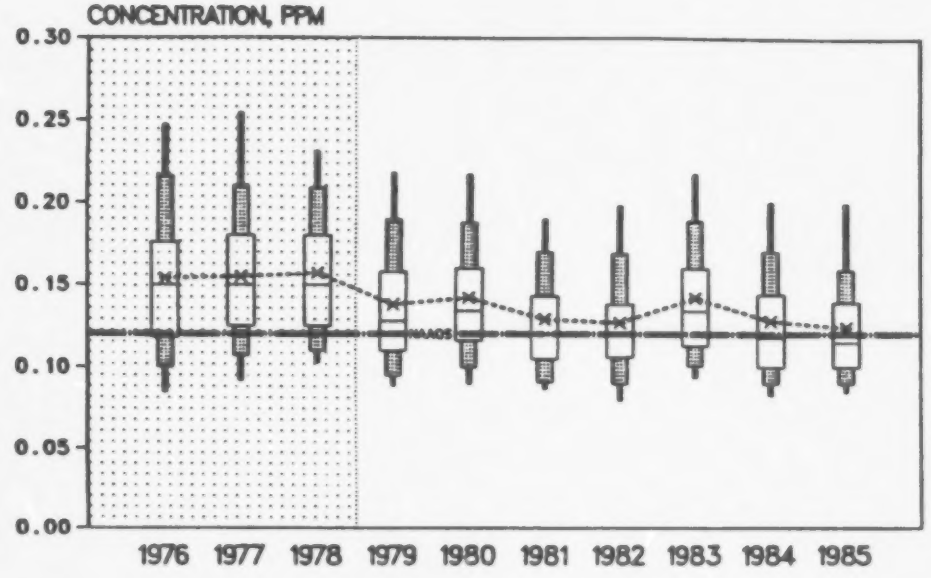


Figure 5. Boxplot comparisons of trends in annual second highest daily maximum 1-hour ozone concentration at 183 sites, 1976-1985.

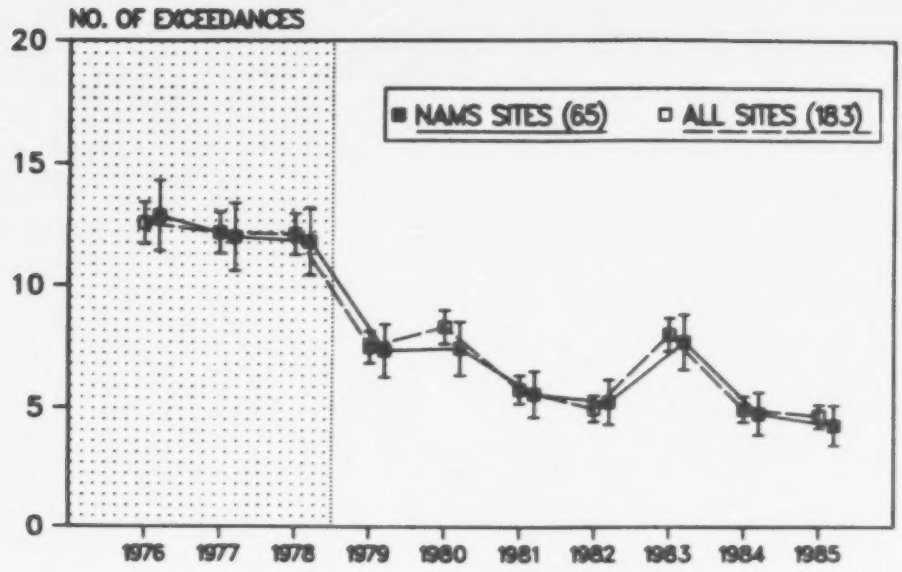


Figure 6. National trend in the composite average of the estimated number of daily exceedances of the ozone NAAQS in the ozone season at both NAMS and all sites with 95 percent confidence intervals, 1976-1985.

Table 1. National Volatile Organic Compound Emission Estimates, 1976-1985.

(million metric tons/year)

| Source Category | 1976 | 1977 | 1978 | 1979 | 1980 | 1981 | 1982 | 1983 | 1984 | 1985 |
|---|---|---|---|---|---|---|---|---|---|---|
| Transportation | 10.3 | 10.0 | 9.7 | 8.9 | 8.2 | 7.9 | 7.4 | 7.3 | 7.3 | 7.2 |
| Fuel Combustion | 1.2 | 1.4 | 1.6 | 1.9 | 2.2 | 2.3 | 2.5 | 2.6 | 2.6 | 2.6 |
| Industrial Processes | 8.7 | 9.1 | 9.7 | 9.6 | 9.0 | 8.1 | 7.3 | 7.7 | 8.6 | 8.6 |
| Non-Industrial Organic Solvent Use | 1.9 | 1.9 | 1.9 | 2.0 | 1.9 | 1.6 | 1.5 | 1.6 | 1.8 | 1.6 |
| Solid Waste | 0.8 | 0.8 | 0.8 | 0.7 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Miscellaneous | 1.0 | 0.8 | 0.8 | 0.9 | 1.0 | 0.9 | 0.7 | 1.1 | 0.9 | 0.7 |
| Total | 24.0 | 23.9 | 24.5 | 24.1 | 22.8 | 21.5 | 20.0 | 20.8 | 21.8 | 21.3 |

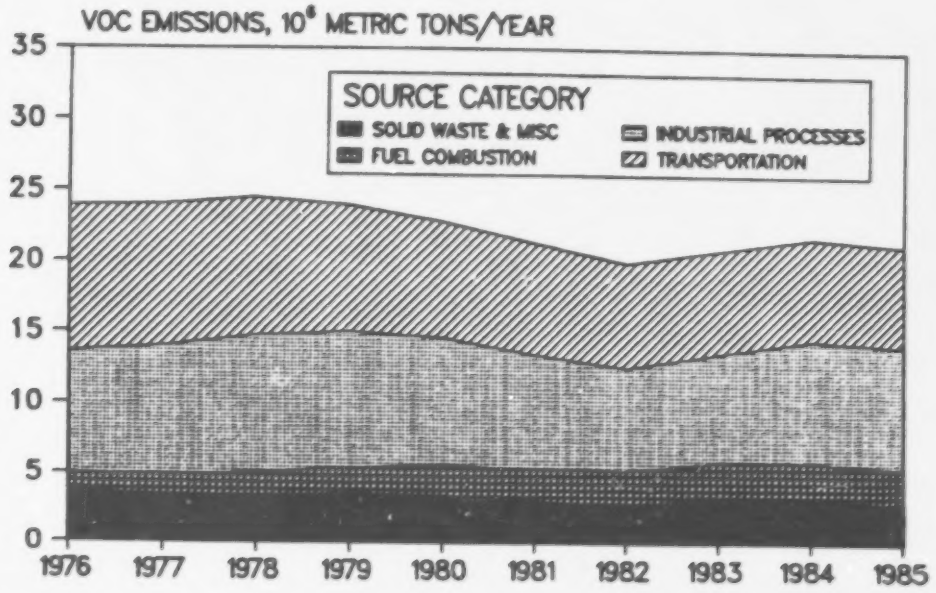


Figure 7. National trend in emissions of volatile organic compounds, 1976-1985.

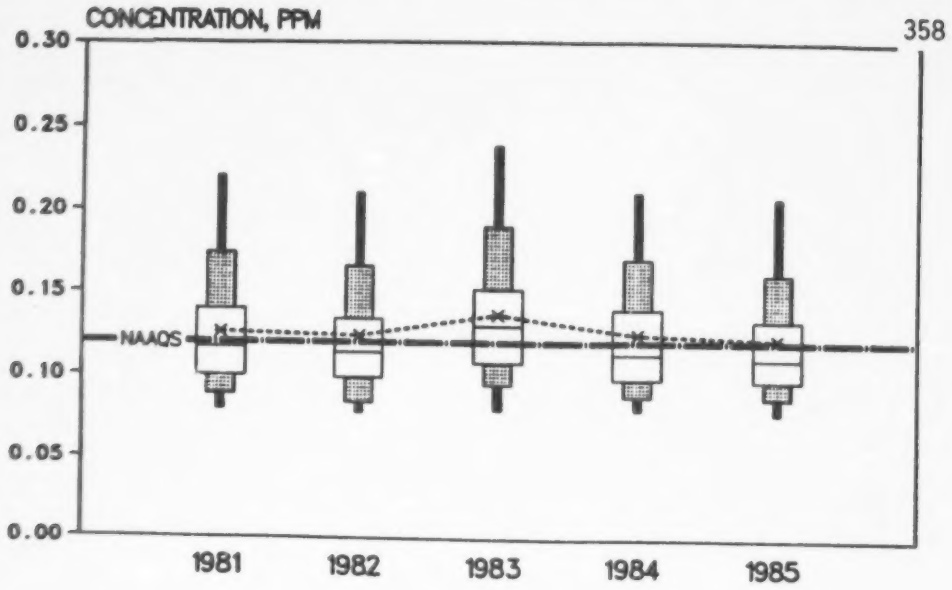


Figure 8. Boxplot comparisons of trends in annual second highest daily maximum 1-hour ozone concentrations at 523 sites, 1981-1985.

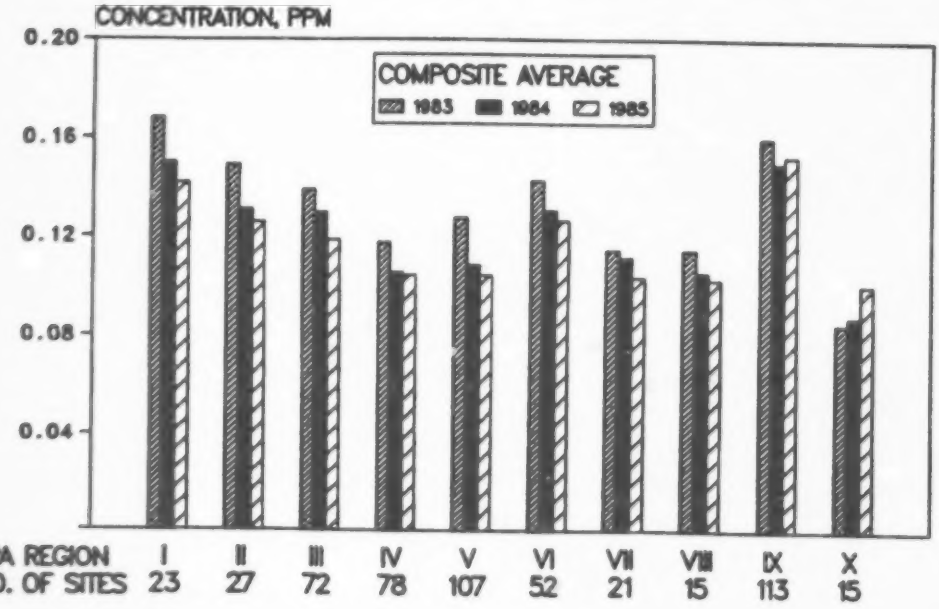


Figure 9. Regional comparison of the 1983, 1984, 1985 composite average of the second-highest daily 1-hour ozone concentrations.

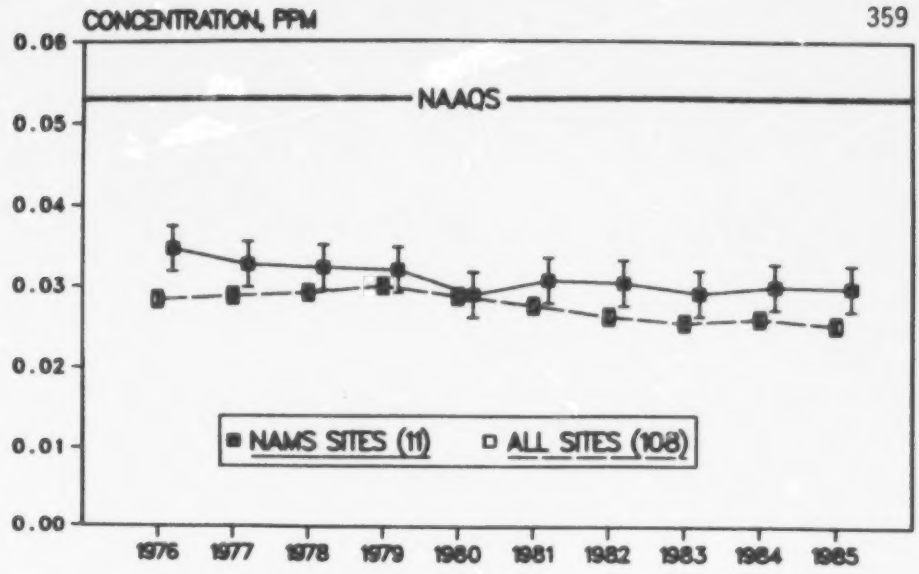


Figure 10. National trend in the composite average of nitrogen dioxide concentration at both NAMS and all sites with 95 percent confidence intervals, 1976-1985.

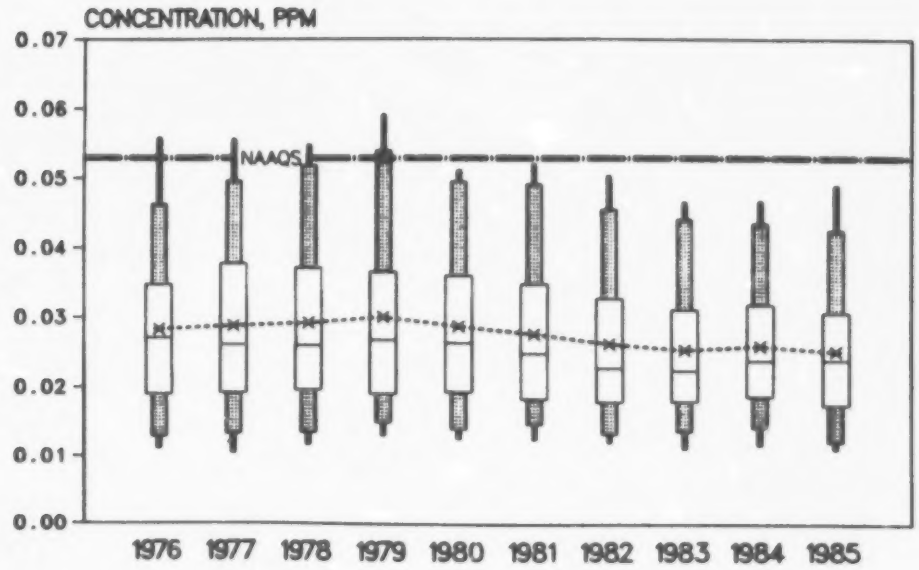


Figure 11. Boxplot comparisons of trends in annual mean nitrogen dioxide concentrations at 108 sites, 1976-1985.

Table 2. National Nitrogen Oxides Emission Estimates, 1976-1985.

(million metric tons/year)

| Source Category | 1976 | 1977 | 1978 | 1979 | 1980 | 1981 | 1982 | 1983 | 1984 | 1985 |
|---|---|---|---|---|---|---|---|---|---|---|
| Transportation | 9.3 | 9.5 | 9.7 | 9.5 | 9.2 | 9.3 | 8.9 | 8.6 | 8.7 | 8.9 |
| Fuel Combustion | 10.0 | 10.4 | 10.3 | 10.5 | 10.1 | 10.0 | 9.8 | 9.6 | 10.2 | 10.2 |
| Industrial Processes | 0.7 | 0.7 | 0.8 | 0.8 | 0.7 | 0.6 | 0.5 | 0.5 | 0.6 | 0.6 |
| Solid Waste | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Miscellaneous | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.1 | 0.2 | 0.2 | 0.1 |
| Total | 20.3 | 21.0 | 21.1 | 21.0 | 20.3 | 20.3 | 19.5 | 19.1 | 19.7 | 20.0 |

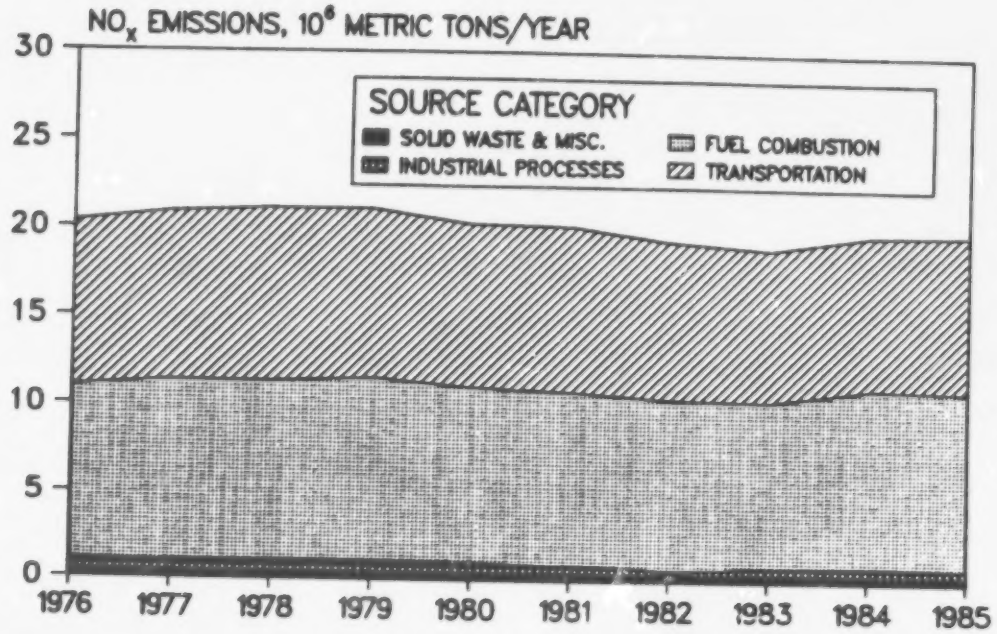


Figure 12. National trend in nitrogen oxides emissions, 1976-1985.

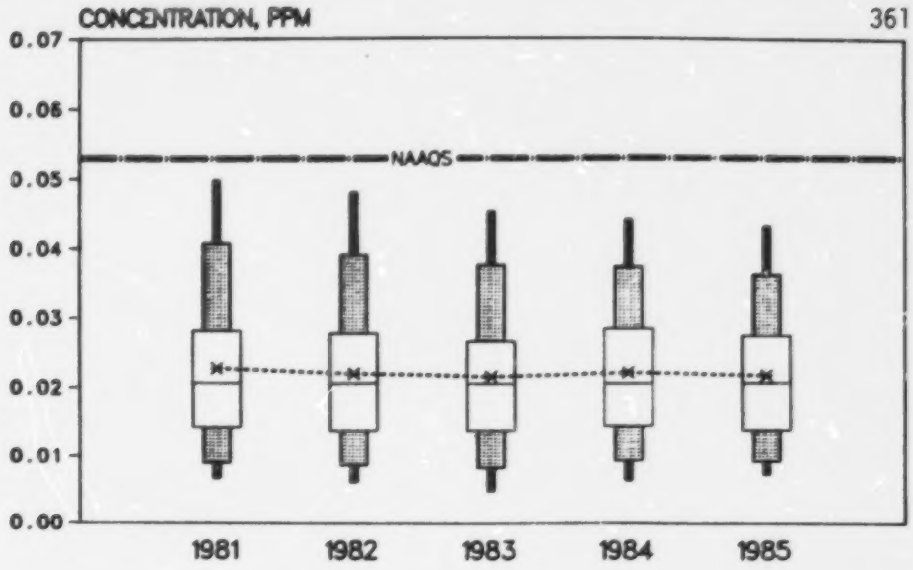


Figure 13. Boxplot comparisons of trends in annual mean nitrogen dioxide concentrations at 243 sites, 1981-1985.

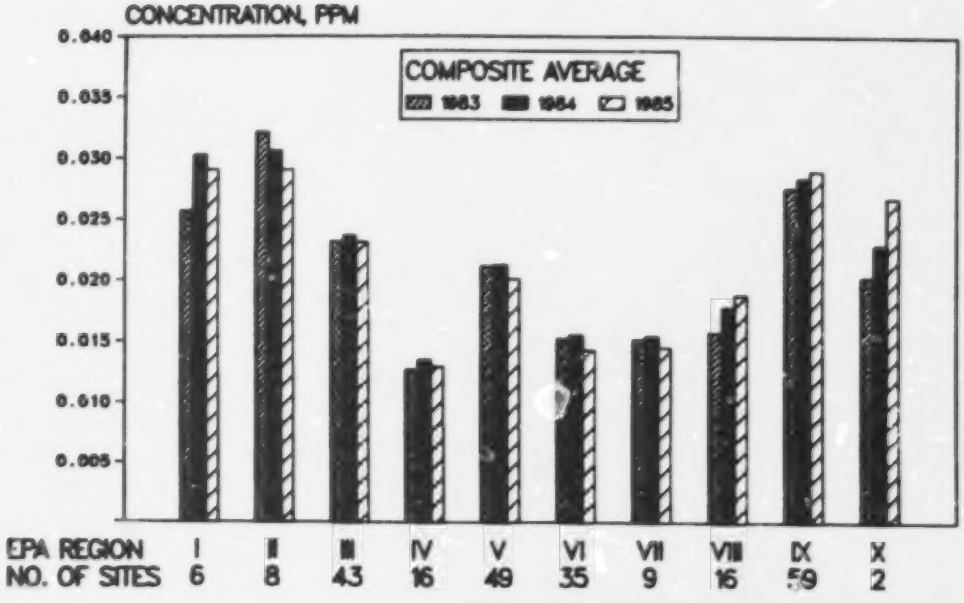


Figure 14. Regional comparison of 1983, 1984, 1985 composite average of the annual mean nitrogen dioxide concentration.

# A REVIEW OF THE ONTARIO OZONE PROBLEMS

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**Air Resources Branch**
**Ontario Ministry of the Environment**

## RÉSUMÉ

Depuis les dix dernières années, l'Air Resources Branch du ministère de l'Environnement de l'Ontario étudie les causes et les effets des épisodes d'ozone en Ontario. Les principales observations des travaux effectués sont résumées dans le présent exposé et les conclusions, présentées ci-dessous.

1. En Ontario, le critère d'ozone de 80 ppb (une heure), qui correspond en gros à un niveau saisonnier moyen de 32 ppb pour sept heures, est souvent dépassé dans le sud-ouest de la province durant la saison chaude, ce qui entraîne des pertes de récolte considérables.

2. Les excès d'ozone se produisent lors de conditions météorologiques connues et sont attribuables aux précurseurs provenant des États-Unis, les émissions de l'Ontario contribuant très peu au problème de la province.

3. Le problème de l'ozone est lié au phénomène du transport à grande distance des polluants atmosphériques qui comprend également les pluies acides et les sulfates.

4. L'Ontario continuera ses efforts en vue d'obliger les États-Unis à réduire sa norme nationale sur la qualité de l'air ambiant de 120 ppb et ses émissions de précurseurs.

5. L'Ontario continuera d'élaborer des stratégies de lutte conjointement avec les États-Unis et d'autres initiatives de sa compétence.

## ABSTRACT

During the past 10 years the Air Resources Branch of the Ontario Ministry of the Environment has been studying the causes and effects of ozone episodes in Ontario. The highlights of the work are summarized in this paper which concludes with the follcwing points:

1. The Ontario ozone criterion of 80 PPB (1 HOUR), which roughly corresponds to a 7-hour seasonal mean level of 32 PPB, is frequently exceeded in Southwestern Ontario in the warm season, resulting in significant crop yield losses.

2. Ozone exceedances occur under known meteorological conditions primarily as the result of precursors from the U.S., with Ontario emissions contributing only slightly to the Ontario problem.

3. The ozone problem is part of the long range transport of air pollutant phenomenon which also includes acid rain and sulphates.

4. Ontario will continue initiatives toward achieving a lowering of the U.S. National Ambient Air Quality Standard of 120 PPB, and reductions in U.S. precursor emissions.

5. Ontario will continue the development of abatement strategies consonant with U.S. and other jurisdictional initiatives.

In this paper, I plan to present some Ontario ozone data, look at the trends, then review albeit selectively, the past ten years of ozone work at the Air Resources Branch.

Table 1 lists the gases which have criteria in Ontario. The criteria are indicated in the final column, and the number of exceedances of these criteria is shown in the second column. Ozone is the most problematic criterion pollutant in Ontario with thirty five of forty one stations recording exceedances of the criterion in 1985. (The criterion, as indicated, is .08 ppm). For Nitrogen Dioxide, nome of the stations had exceedances. For Sulfur Dioxide, 17 statioms of 83 had exceedances.

All of the 40 ozone monitors in Ontario are indicated in Figure 1. Figure 2 is a close-up for Southern Ontario which has 27 monitors. The monitors are situated in both urban and rural locations; the largest urban location is the Toronto-Hamilton area.

The reference level for ozone in Ontario is the ozone criterion of 80 ppb for 1 hour. An ozone exceedance is defined as a value in excess of 80 ppb. All southwestern Ontario stations record exceedances of ozone on a regular basis (see Figure 3). The number of exceedances decreases from south to north, but there is much variability in the Toronto-Hamilton area because ozone is simultaneously being produced from precursors and scavenged by Nitric Oxide in this area. The highest number of exceedances in the province is usually at Longpoint on a peninsula extending eastward into Lake Erie. The number of exceedances between 1983 and 1985 was 504. The six stations with the most exceedances between 1983 and 1985 are shown in Figure 4.

The 1985 distribution by month is shown in Table 2, indicating most exceedances in June and July. There is considerable variability in the seasonal distribution from year to year.

We have compared the levels measured in southern Ontario with other jurisdictions, for example the Federal Republic of Germany (see Table 3).[1] Apart from Schauinsland, the number of

hours of exceedances of the 80 ppb reference level, and the maximum values, are comparable to the Southern Ontario stations.

We looked at long-term variations and Table 4 shows the annual mean (for all 8760 hours of the year) for 10 years. It shows the lack of strong trends in the southern Ontario data. It shows also that 1978 appeared to have a significantly higher average relative to the other 9 years. If we select the warm season daylight hours (Table 5), we see that 1978 stands out even further. Figure 5 depicts ozone exceedances in the ten-year period between 1976 and 1985.(Whiteface Mountain is black and Simcoe is hatched). Again 1978 stands out as a maximum for both locations, and there is general agreement between the number of exceedances observed at Simcoe, Ontario and Whiteface Mountain, New York.(1)

To better understand the ozone phenomenon, we studied widespread occurrences of high ozone which we called ozone episodes. These occurrences, typically covering hundreds of kilometres(2), are defined as one or more days of ozone greater than 80 ppb at 8 or more stations. An ozone episode-day is defined as one day of an ozone episode. An ozone episode might typically consist of several episode days.

In summarizing ten years of data for ozone episodes and ozone episode-days (Table 6), 1978 stood out with a very high number of both ozone episodes and ozone episode-days. Further study was done of ozone episodes of particularly long duration, that is three days or more. Table 7 gives the duration in days for each of these episodes. In 1976 for example, there was a three day episode in June and a three day episode in August. In 1978 there were a large number of ozone episodes and ozone episode days. This table points out that the higher than average 1983 data were heavily influenced by a single eight day episode which occurred in June.

We were able to produce an ozone climatology for the ten-year period (Table 8). We found that 63 ozone episodes consisted of a single day; 24 consisted of 2 days and so on. There was one episode which lasted 8 days.

That gave a total of 106 episodes and 185 episode days. Table 9 shows the expected number of episodes in each month; there are no expected episodes outside of the period May to September. Various studies done at the Air Resources Branch have demonstrated the meteorological conditions required for ozone episodes. These are summarized in Table 10.

Trajectory analysis indicated that source regions to the south and south-west, were impacting on southwestern Ontario during episodes. Figure 6 shows 48 hour back-trajectories, based on a surface geostrophic model with frictional corrections.(4)

Figure 7 is a classic ozone pattern, which was recorded by Wolff and Lioy in 1977.(5) It indicates that episodes do not occur in Ontario in isolation. Normally southwestern Ontario is the extreme northerly edge of a so-called ozone river, which may sweep around an area of high pressure.(6,7) In this particular case, there were two high pressure centres, one just south of Lake Ontario and one over the southeastern US.

The manifestation of an ozone episode at a particular location is shown in Figure 8 for the Summer of 1984. The plots are for Simcoe, Ontario, Whiteface Mountain, and Arzberg, Germany. The diurnal patterns in Ontario and West Germany are not dissimilar. Whiteface Mountain shows a type of diurnal variation, actually not much variation at all, typical of a mountain location. There is a slight dip during the late morning hours and a maximum near midnight.

The typical diurnal variation is caused by the nocturnal inversion, which isolates the ozone above the ground.(1) The same kind of pattern can be seen in the number of ozone exceedances for each hour of the day (Figure 9). This particular plot shows the sum of ozone exceedances during a 5 year period at three locations, and has a maximum at 5 in the afternoon and a minimum around 8 in the morning.

We have spoken so far of 80 ppb hourly exceedances, but the best documented effect of high ozone in Ontario, is related to damage to sensitive crops. The National Crop Loss Assessment Network, NCLAN, has recommended that the 7 hour seasonal mean for ozone (9 am to 4 pm) is the most relevant measure of ozone impact on crops.(8)

Thirty ppb, as a 7 hour seasonal mean, has been shown to produce little or no damage to crops. Forty ppb on the other hand, results in significant yield loses in sensitive crops. Our phyto-toxicological section has found a good correlation between a criterion of 80 ppb for 1 hour and a 7 hour seasonal mean criterion of 32 ppb. That is to say: if one criterion is met, so is the other. If one of them is not met, neither is the other.

The 7 hour seasonal mean in three different jurisdictions is shown in Figure 10. Basically what we find is that a 7 hour seasonal mean of 32 ppb, above which yield losses are expected, is regularly exceeded in southwestern Ontario as it is at Whiteface Mountain, and in Hohenpeissenberg, Germany.

The exceedances of these criteria, whether we speak of the 80 ppb (1 hour max) or the 7 hour seasonal mean of 32 ppb, result in crop yield losses valued at about 20 million dollars.(8)

Let me now briefly enter the precursor control strategy debate. Table 11 shows the 1983 estimated anthropogenic ozone precursor emissions. The total mass emissions of NOx and NMHC are almost identical. That translates roughly into a molar ratio between NMHC and NOx of 3:1. With reference to Dr. Dodge's comments(13) on the type of control required, as a function of that ratio, Ontario should be pursuing non-methane hydrocarbon control.

At the bottom of Table 11, we indicate the NOx and NMHC emissions in 13 northeast states which impact most on Ontario.(9,10,11) They are the 13 states from which most of the back trajectories

originate. For those states, the molar ratio of anthropogenic non-methane hydrocarbons to NOx is roughly 5:1. Again NMHC control would seem in order.

The natural emissions for non-methane hydrocarbons are very large in Ontario, in comparison with the anthropogenic NMHC emissions (see Table 11). If we look at the ratio between total NMHC, including both anthropogenic and natural NMHC, we find a ratio of about 60:1. For Ontario as a whole then, we might reach quite a different conclusion with respect to the type of strategy required for effective downwind ozone control.

Figure 11 depicts the EKMA curves([12]). The major source regions of Ontario lie roughly in the portion indicated by the large dot. It is clear that NMHC control (i.e. moving leftward from the dot) is much more effective than NOx control (moving downward from the dot) which will in many cases exacerbate the problem.

After one determines the type of strategy to use, different approaches would be required in different urban areas depending on the major source of each of the precursors.

These are the broad conclusions to date of the oxidant program: The Ontario ozone criterion of 80 ppb for 1 hour, which corresponds to a 7 hour seasonal mean of 32 ppb, is frequently exceeded in southwestern Ontario in the warm season, resulting in significant crop yield losses.

Ozone exceedances occur under known meteorological conditions, primarily as the result of precursors from the US, with Ontario emissions contributing only slightly to the Ontario problem but very likely contributing to the overall eastern North America problem.

Ozone is part of the long range transport of air pollutants phenomenon which includes acid rain and sulphates.

Ontario will continue initiatives toward achieving a lowering of the US National Ambient Air Quality Standard of 120 ppb. This, notwithstanding Dr. Rao's finding([13]) that the most ambitious control strategies will not produce compliance with the current NAAQS standard.

Finally, Ontario will continue the development of abatement strategies which are in harmony with US and other jurisdictional initiatives.

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R-MAR31

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13. Reference is to other papers presented at this conference.

TABLE 1

NUMBER OF ONTARIO STATIONS

RECORDING

CRITERIA EXCEEDANCES

1985

| | NUMBER | TOTAL NO. STATIONS | CRITERION |
|---|---|---|---|
| $SO_2$ | 17 | 83 | 0.25 |
| CO | 1 | 26 | 30 |
| $NO_2$ | 0 | 33 | 0.20 |
| $O_3$ | 35 | 41 | 0.08 |

TABLE 2

MONTHLY DISTRIBUTION FOR STATIONS WITH
OVER 50 OZONE EXCEEDANCES
1985

| | LONG POINT | THEDFORD | TIVERTON | WINDSOR | SIMCOE |
|---|---|---|---|---|---|
| JAN | | | | | |
| FEB | | | | | |
| MAR | | | | | |
| APR | 14 | 9 | 10 | | 6 |
| MAY | 36 | 17 | 23 | 10 | 20 |
| JUNE | 18 | 5 | 9 | 12 | 13 |
| JUL | 81 | 25 | 23 | 36 | 32 |
| AUG | 24 | 19 | 9 | 12 | - |
| SEPT | 10 | 17 | 12 | 7 | - |
| OCT | | | | | |
| NOV | | | | | |
| DEC | | | | | |
| TOTAL | 183 | 92 | 86 | 77 | 71+ |

TABLE 3

COMPARISON OF RURAL OZONE EXCEEDANCES
IN ONTARIO AND WEST GERMANY
1982-1984

| WEST GERMANY | No. HRS. | MAX. | ONTARIO | No.HRS. | MAX. |
|---|---|---|---|---|---|
| SCHAUINSLAND | 1091 | 133 | Long Point | 452 | 136 |
| BROTJACKLRIEGEL | 584 | 122 | Simcoe | 426 | 123 |
| WALDHOF | 565 | 160 | Huron Park | 196 | 125 |
| HOHENPEISSENBERG | 178 | 133 | | | |

(FROM LEFOHN AND MOHNEN)

TABLE 4

TEN YEAR OZONE TREND (PPB)
18 SITES
ANNUAL MEAN

| 1976 | 1977 | 1978 | 1979 | 1980 |
|---|---|---|---|---|
| 20 | 20 | 23 | 20 | 20 |

| 1981 | 1982 | 1983 | 1984 | 1985 |
|---|---|---|---|---|
| 19 | 20 | 20 | 20 | 21 |

TABLE 5

TEN YEAR OZONE TREND (PPB)
18 SITES
WARM SEASON - DAYLIGHT HOURS

| 1976 | 1977 | 1978 | 1979 | 1980 |
|---|---|---|---|---|
| 35 | 34 | 39 | 32 | 32 |
| 1981 | 1982 | 1983 | 1984 | 1985 |
| 31 | 31 | 34 | 33 | 31 |

TABLE 6

HISTORY OF OZONE EPISODES
(AND EPISODE-DAYS)
IN ONTARIO

| 1976 | 1977 | 1978 | 1979 | 1980 |
|---|---|---|---|---|
| 11(18) | 12(21) | 22(43) | 5(14) | 8(13) |

| 1981 | 1982 | 1983 | 1984 | 1985 |
|---|---|---|---|---|
| 12(18) | 5(7) | 13(25) | 10(17) | 8(9) |

## TABLE 7

### SUMMARY OF OZONE EPISODES OF 3 OR MORE DAYS DURATION

| | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 |
|---|---|---|---|---|---|---|---|---|---|---|
| JAN | | | | | | | | | | |
| FEB | | | | | | | | | | |
| MAR | | | | | | | | | | |
| APRIL | | | | | | | | | | |
| MAY | | 4 | 7 | | | 3 | | | | |
| JUNE | 3 | | | 4 | 4 | | | 8 | | |
| JUL | | 3,3 | 3,5 | 4,4 | | 3 | | | 3 | |
| AUG | 3 | | 3,4,3 | | | | | | | |
| SEPT | | | | | | | | | | |
| OCT | | | | | | | | | | |
| NOV | | | | | | | | | | |
| DEC | | | | | | | | | | |

TABLE 8

DURATION OF OZONE EPISODES
1976-1985

| | FREQUENCY | |
|---|---|---|
| 1 DAY | 63 | |
| 2 DAYS | 24 | |
| 3 DAYS | 10 | |
| 4 DAYS | 6 | |
| 5 DAYS | 1 | |
| 6 DAYS | 0 | |
| 7 DAYS | 1 | |
| 8 DAYS | 1 | |
| | 106 | EPISODES |
| | 185 | EPISODES-DAYS |

TABLE 9

EXPECTED NUMBER OF
OZONE EPISODES PER MONTH
FOR ONTARIO

| | | |
|---|---|---|
| MAY | 0.9 | |
| JUNE | 2.7 | |
| JULY | 3.2 | |
| AUGUST | 1.7 | |
| SEPTEMBER | 0.8 | |
| YEAR | 9.3 | EPISODES |

TABLE 10

METEOROLOGICAL CONDITIONS
FOR
OZONE EPISODES

- REAR OF ANTICYCLONE
- WARM, MOIST AIR
- SOUTH OR SOUTHWEST WINDS

TABLE 11

1983 ONTARIO ANTHROPOGENIC
OZONE PRECURSOR EMISSIONS
(KT/YR)

| | NOx | NMHC | |
|---|---|---|---|
| TRANSPORTATION | 355 | 228 | |
| POINT SOURCES | 191 | 253 | |
| FUEL COMBUSTION | 27 | 96 | |
| OTHER | 23 | 21 | |
| | 596 | 598 | (NATURAL = 13500) |
| 13 NE STATES | 4800 | 6200 | (NATURAL = 9500) |

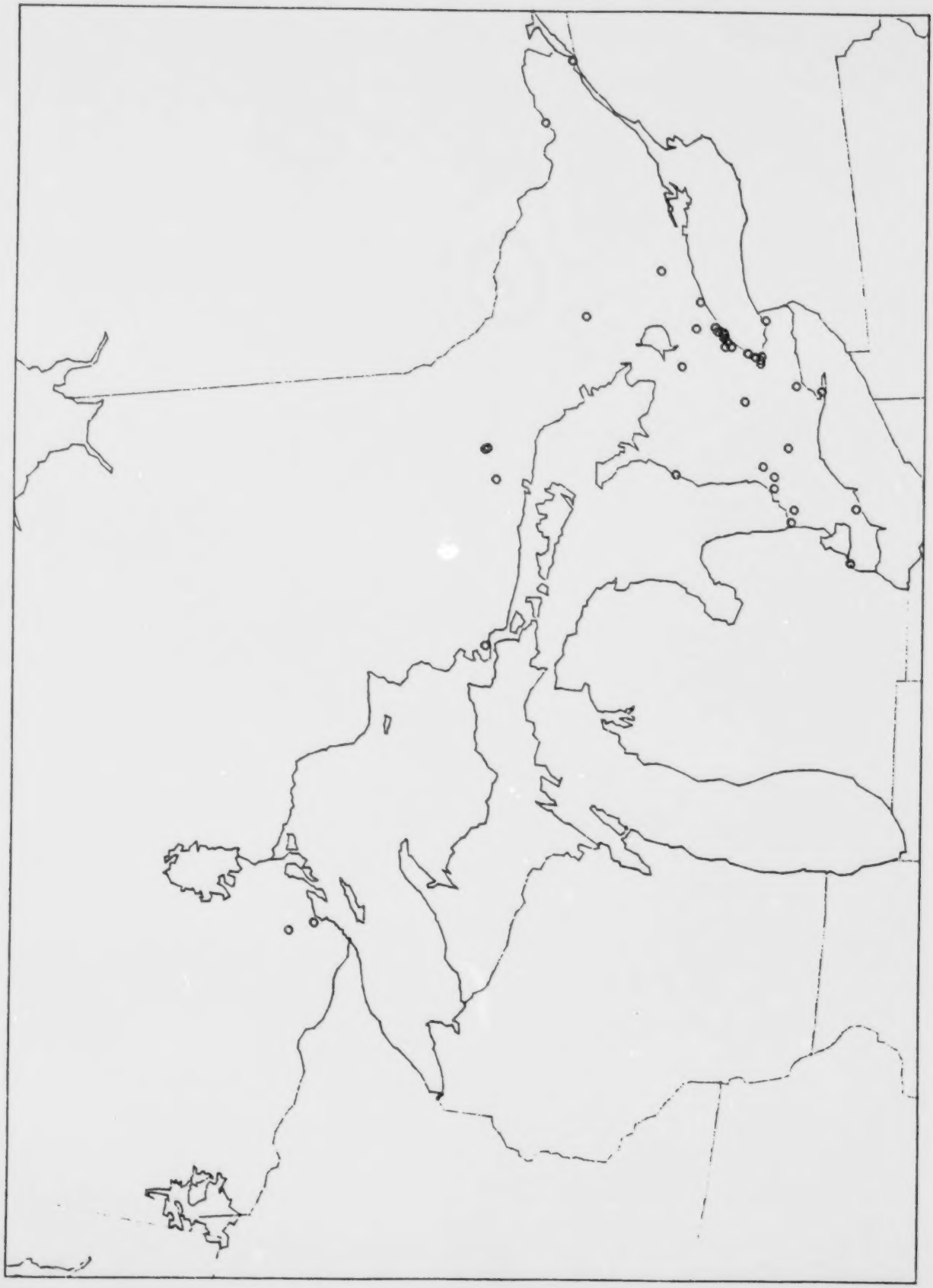


FIGURE 1 ONTARIO'S 40 OZONE MONITORS

FIGURE 2 SOUTHERN ONTARIO'S 27 OZONE MONITORS

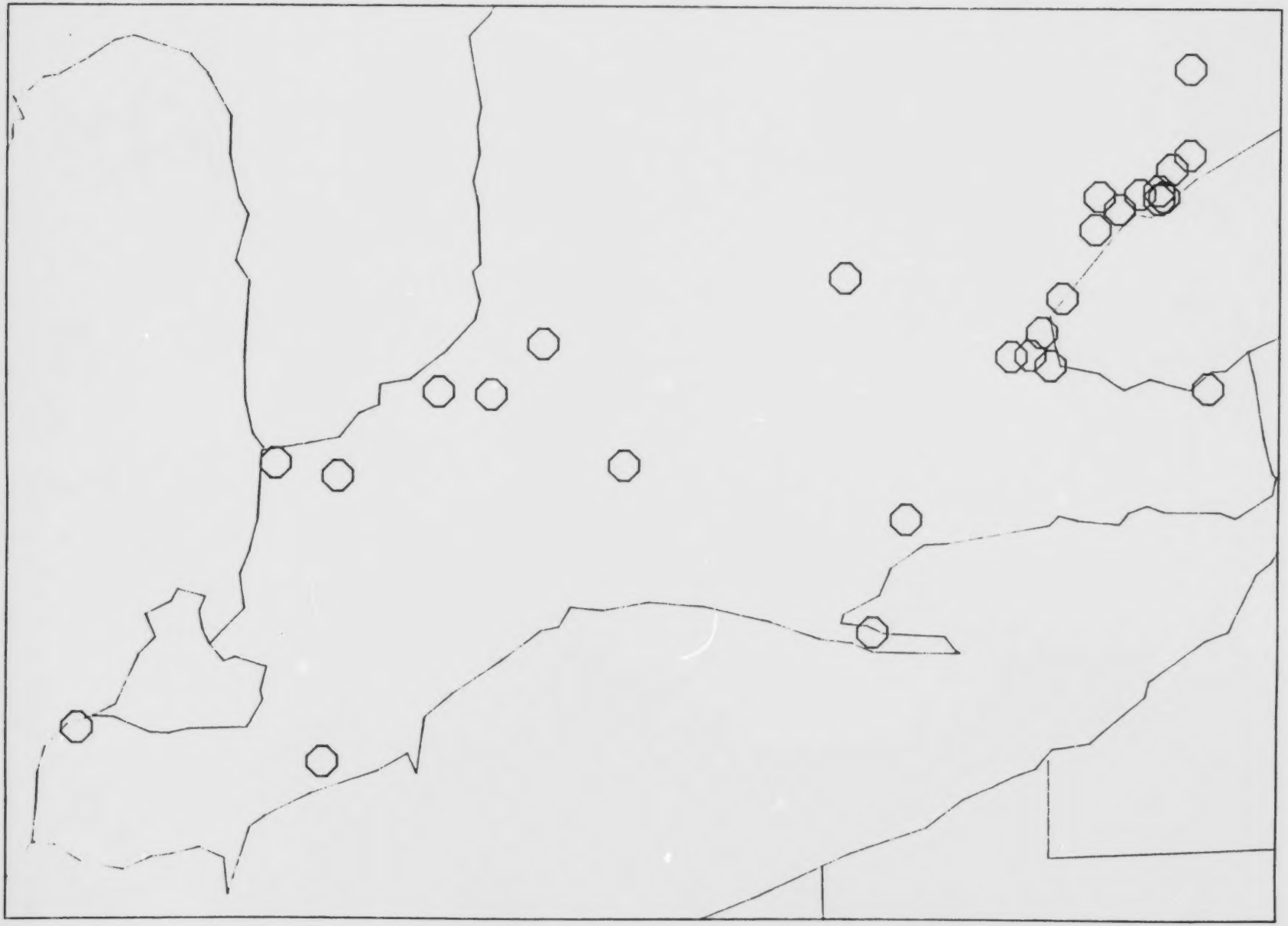


FIGURE 3 TOTAL OF OZONE EXCEEDANCES 1983 - 85

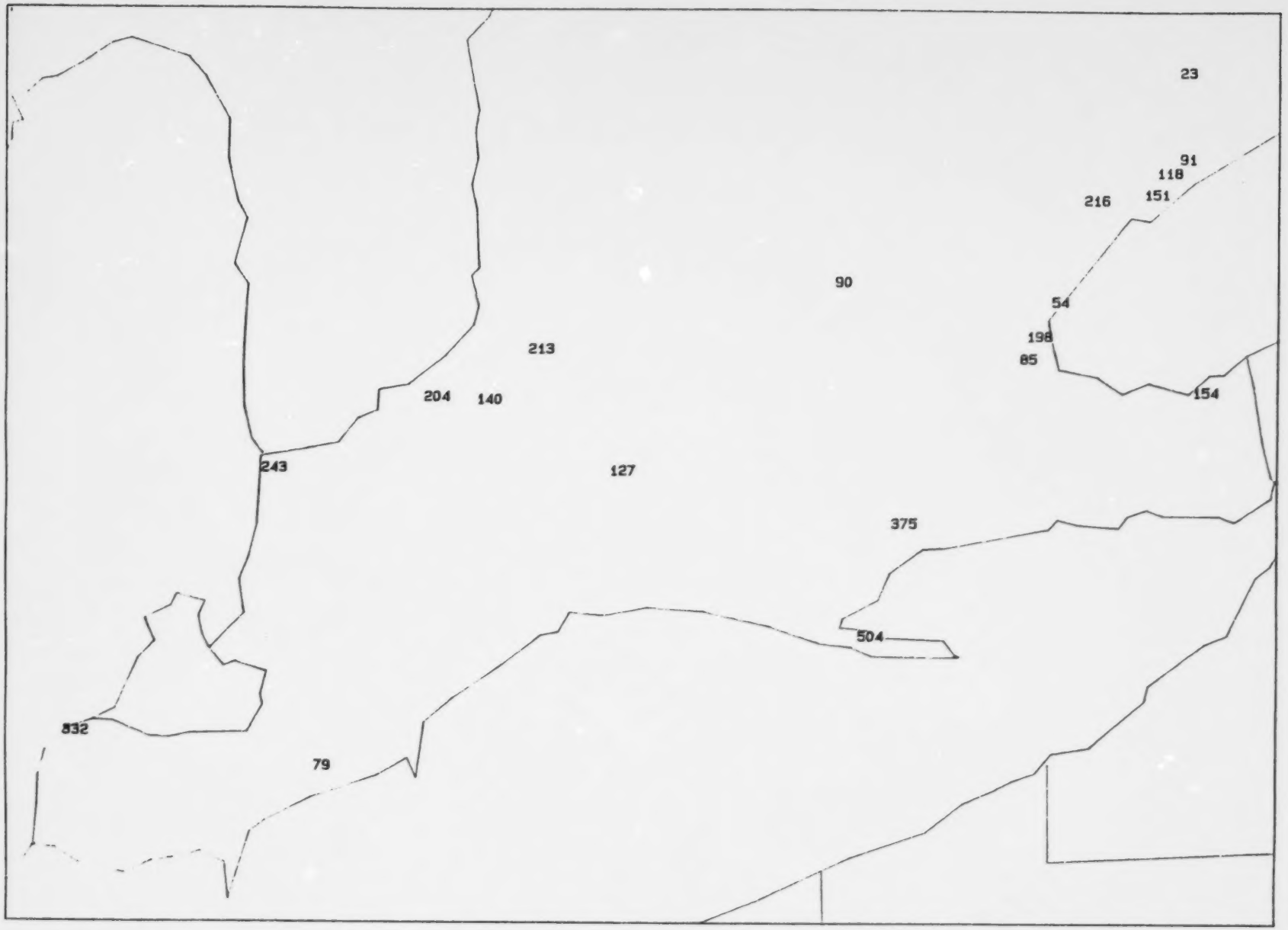


FIGURE 4 ONTARIO STATIONS MEASURING OVER 200 EXCEEDANCES 1983 - 85

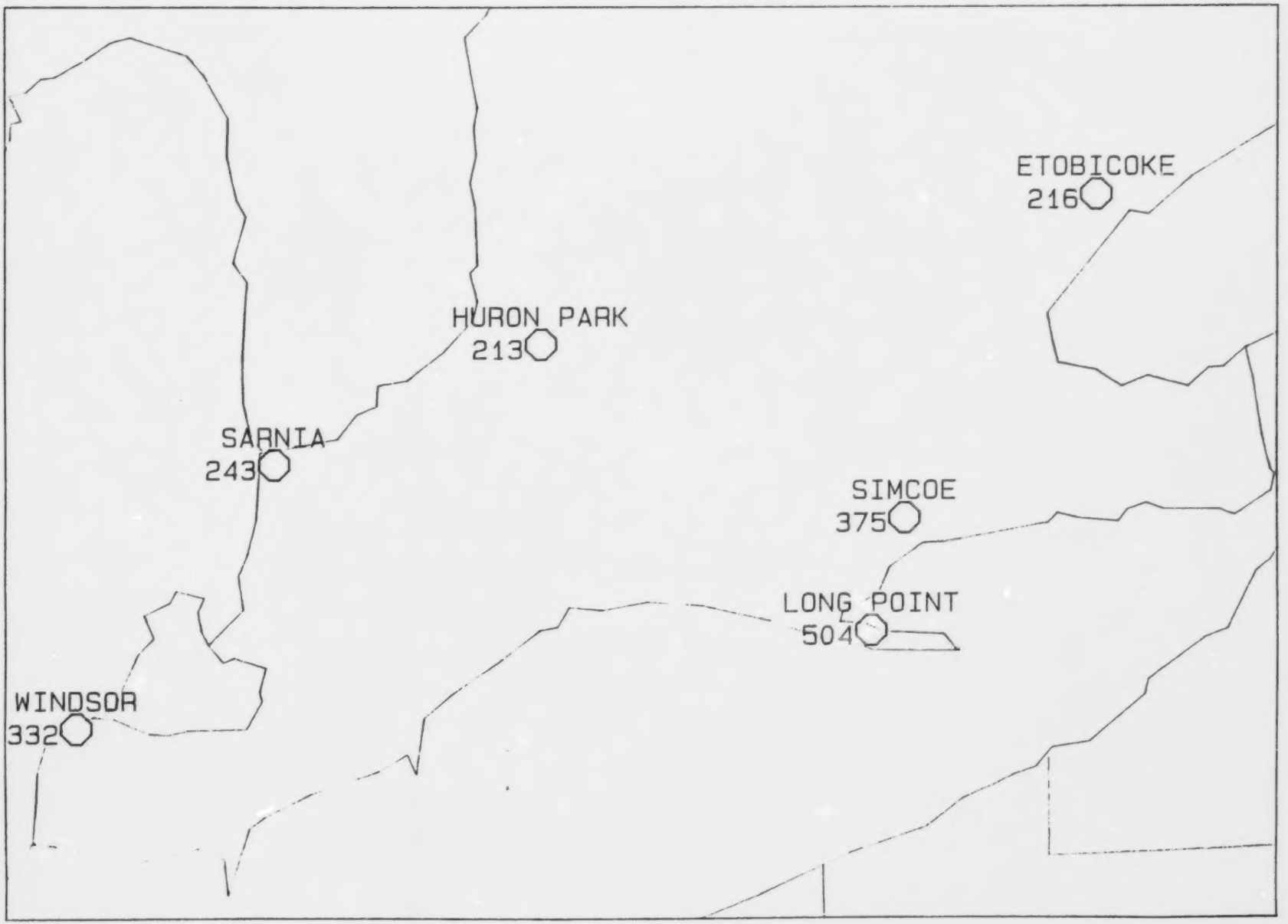


FIGURE 5

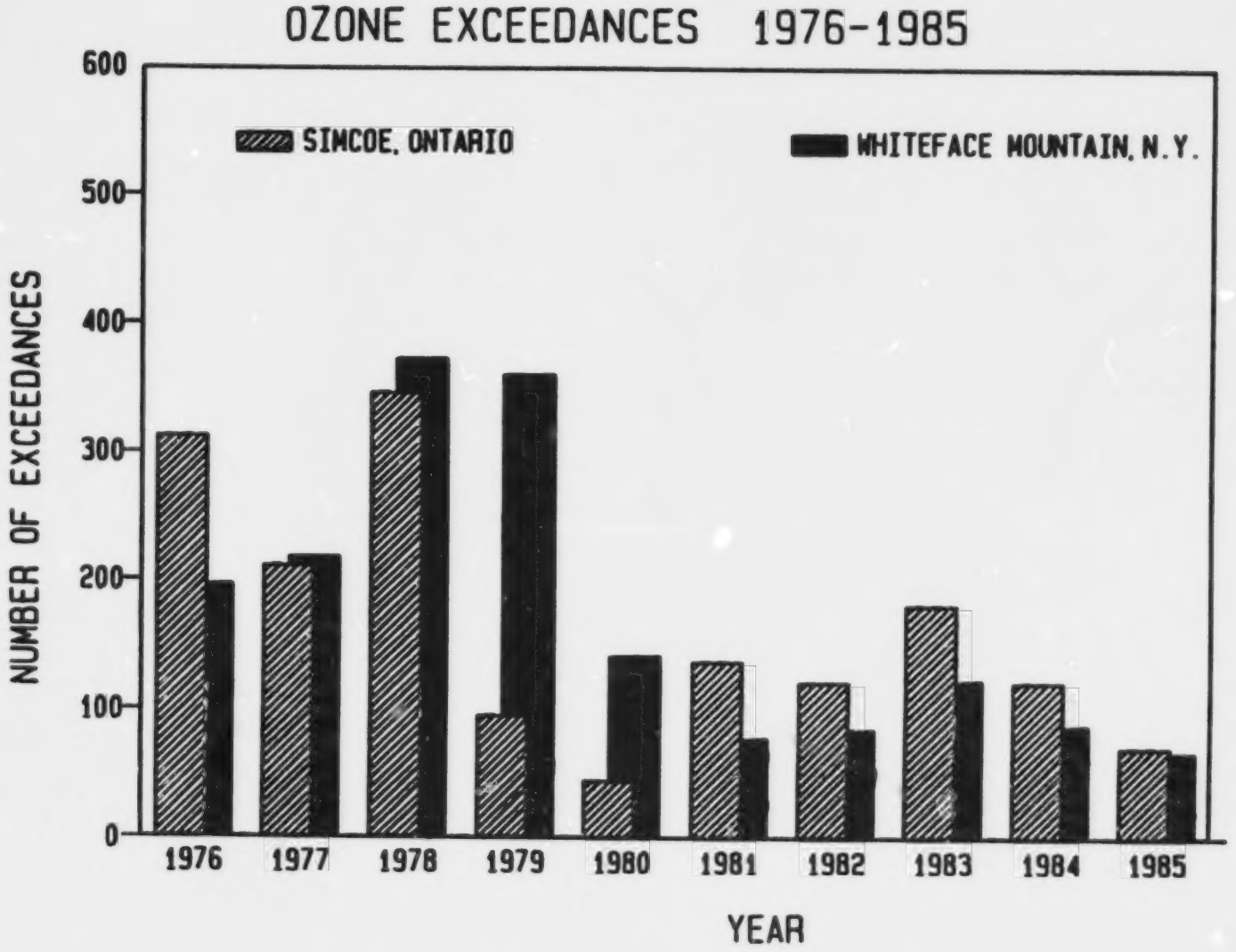

OZONE EXCEEDANCES 1976-1985
SIMCOE, ONTARIO
WHITEFACE MOUNTAIN, N.Y.
NUMBER OF EXCEEDANCES
600
500
400
300
200
100
0
1976
1977
1978
1979
1980
1981
1982
1983
1984
1985
YEAR

FIGURE 6 BACK TRAJECTORIES FROM SOUTHWESTERN ONTARIO FOR 25 OZONE EPISODE - DAYS IN 1983

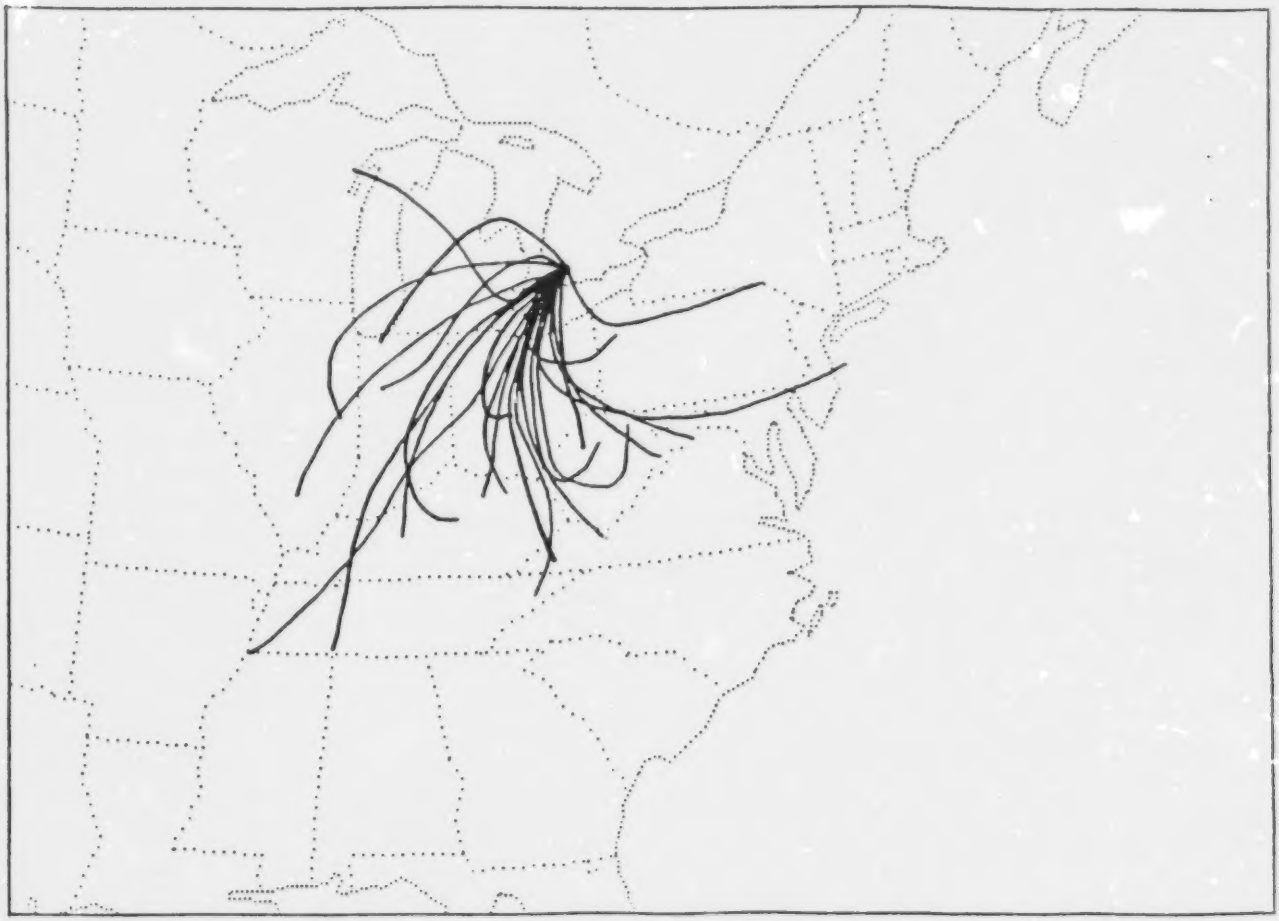


FIGURE 7 OZONE PATTERN FOR JULY 15, 1977

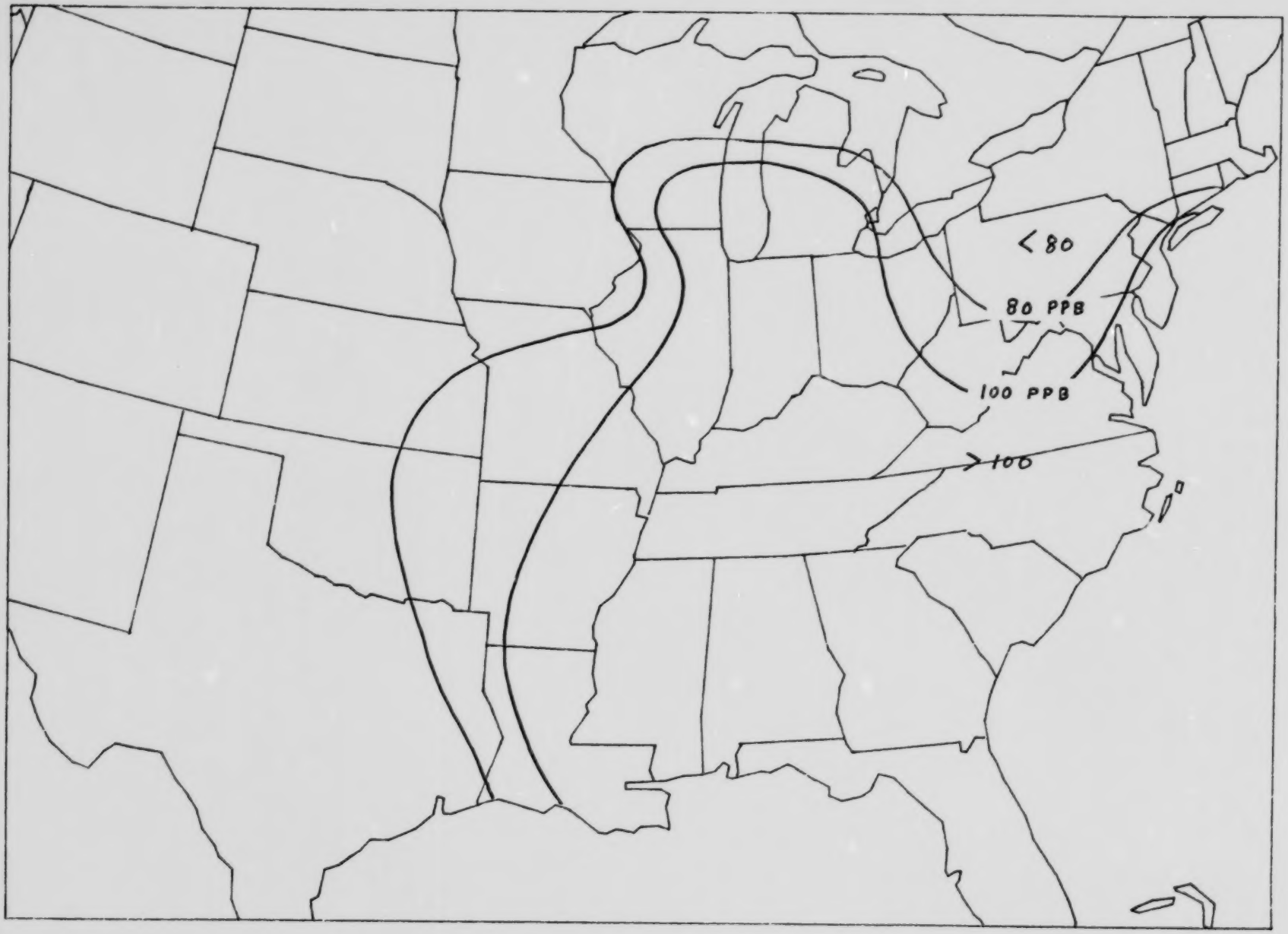


FIGURE 8

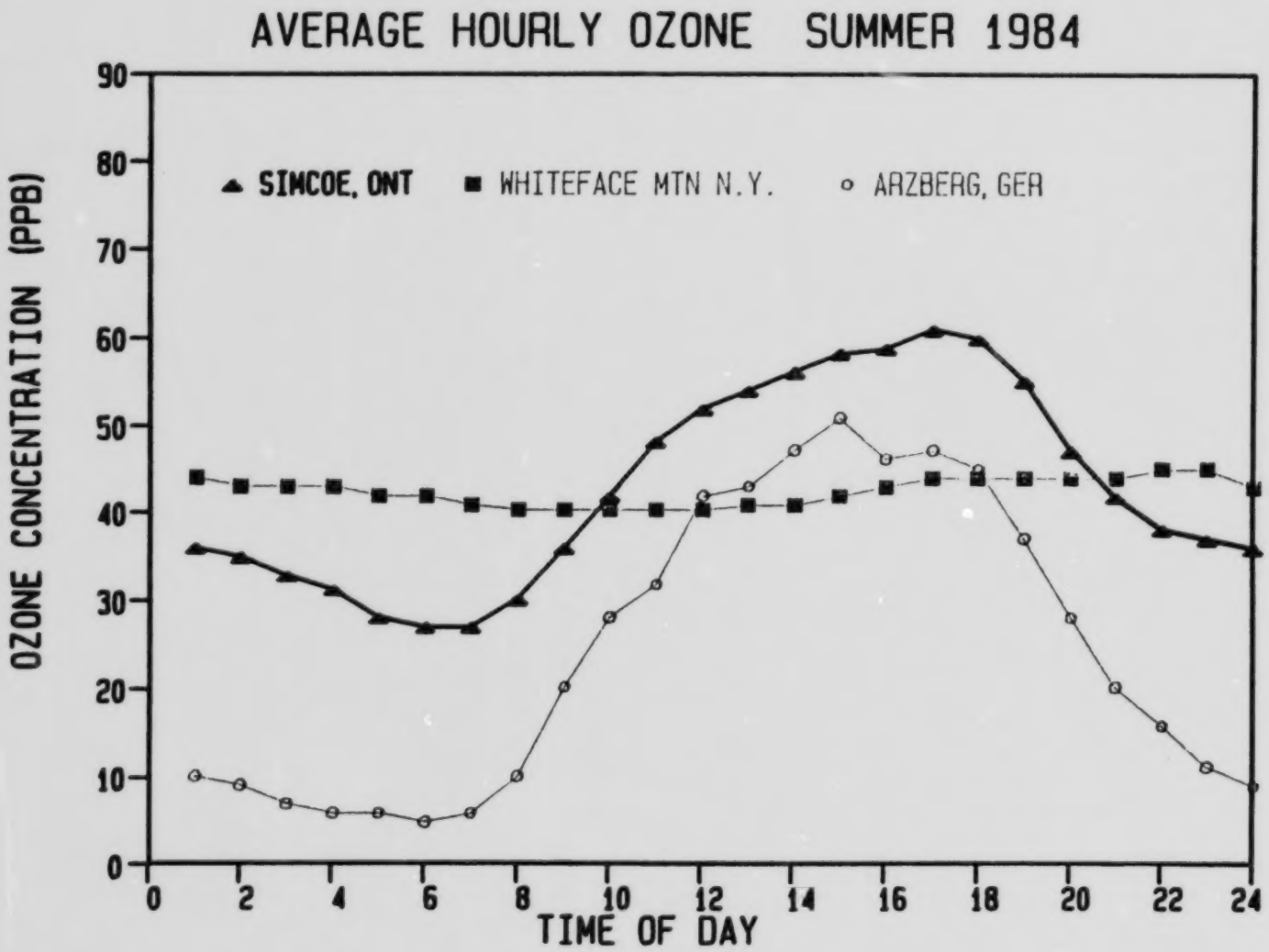

AVERAGE HOURLY OZONE SUMMER 1984
SIMCOE, ONT
WHITEFACE MTN N.Y.
ARZBERG, GER
OZONE CONCENTRATION (PPB)
TIME OF DAY
0
10
20
30
40
50
60
70
80
90
0
2
4
6
8
10
12
14
16
18
20
22
24

FIGURE 9

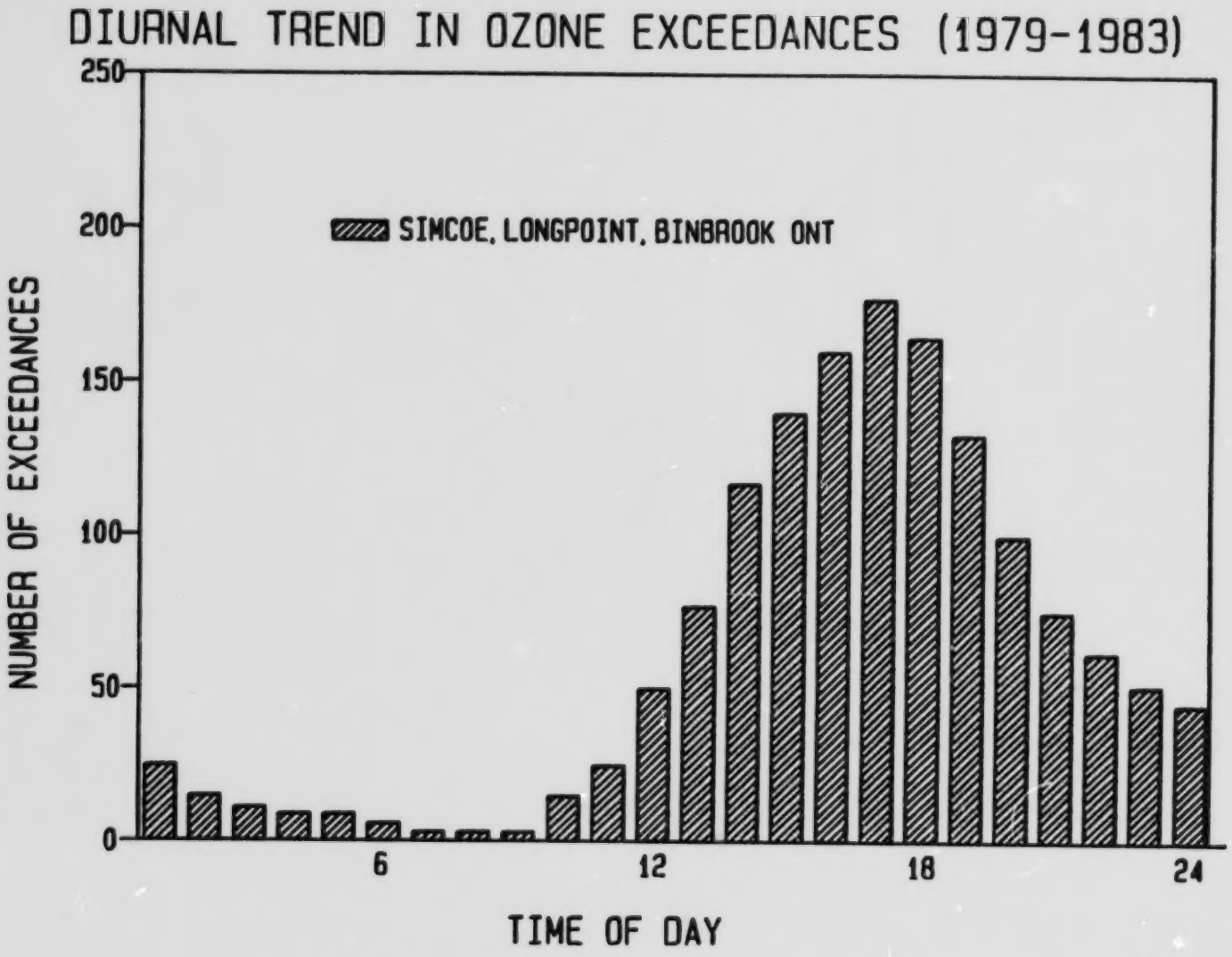

DIURNAL TREND IN OZONE EXCEEDANCES (1979-1983)
SIMCOE, LONGPOINT, BINBROOK ONT
NUMBER OF EXCEEDANCES
250
200
150
100
50
0
6
12
18
24
TIME OF DAY

FIGURE 10

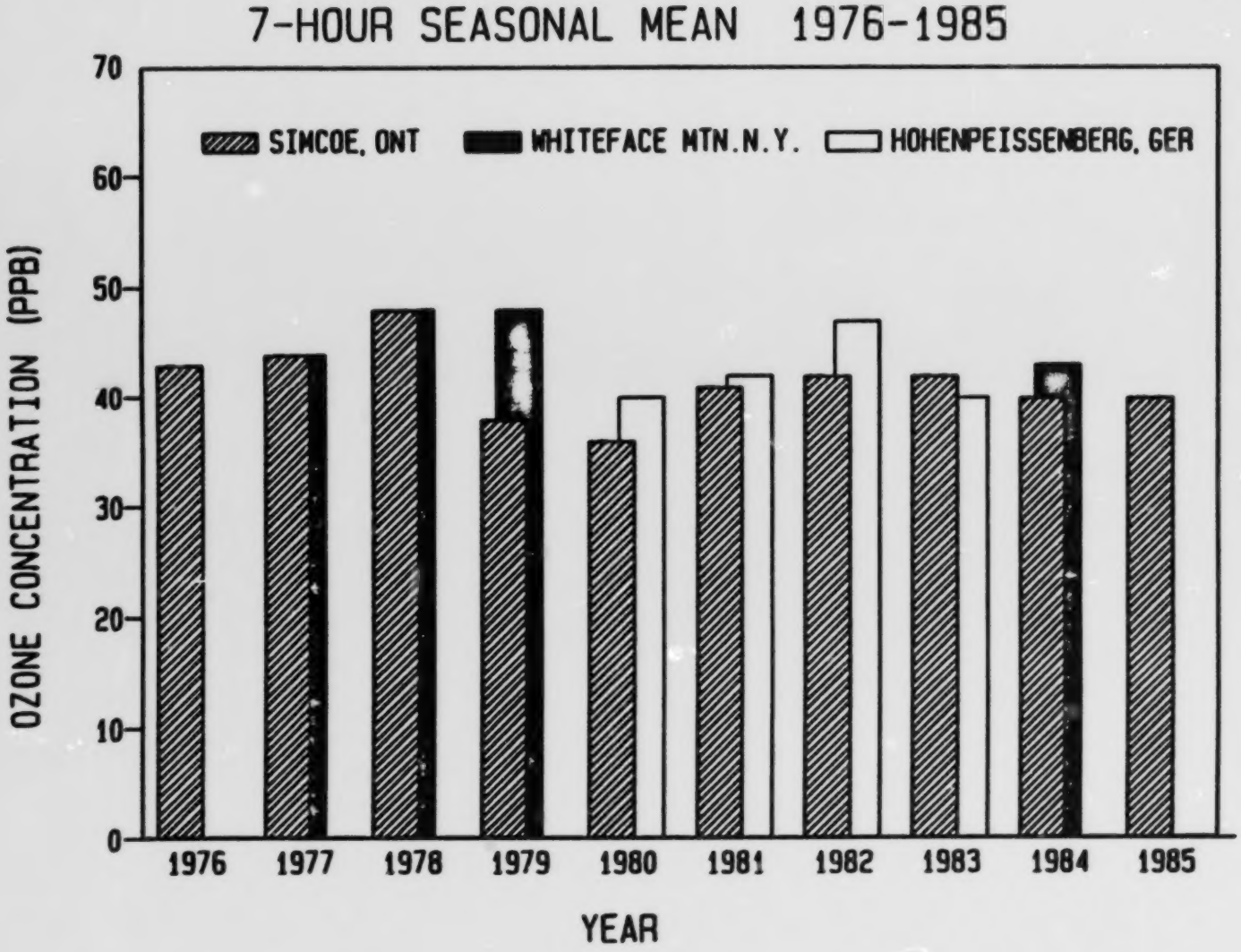
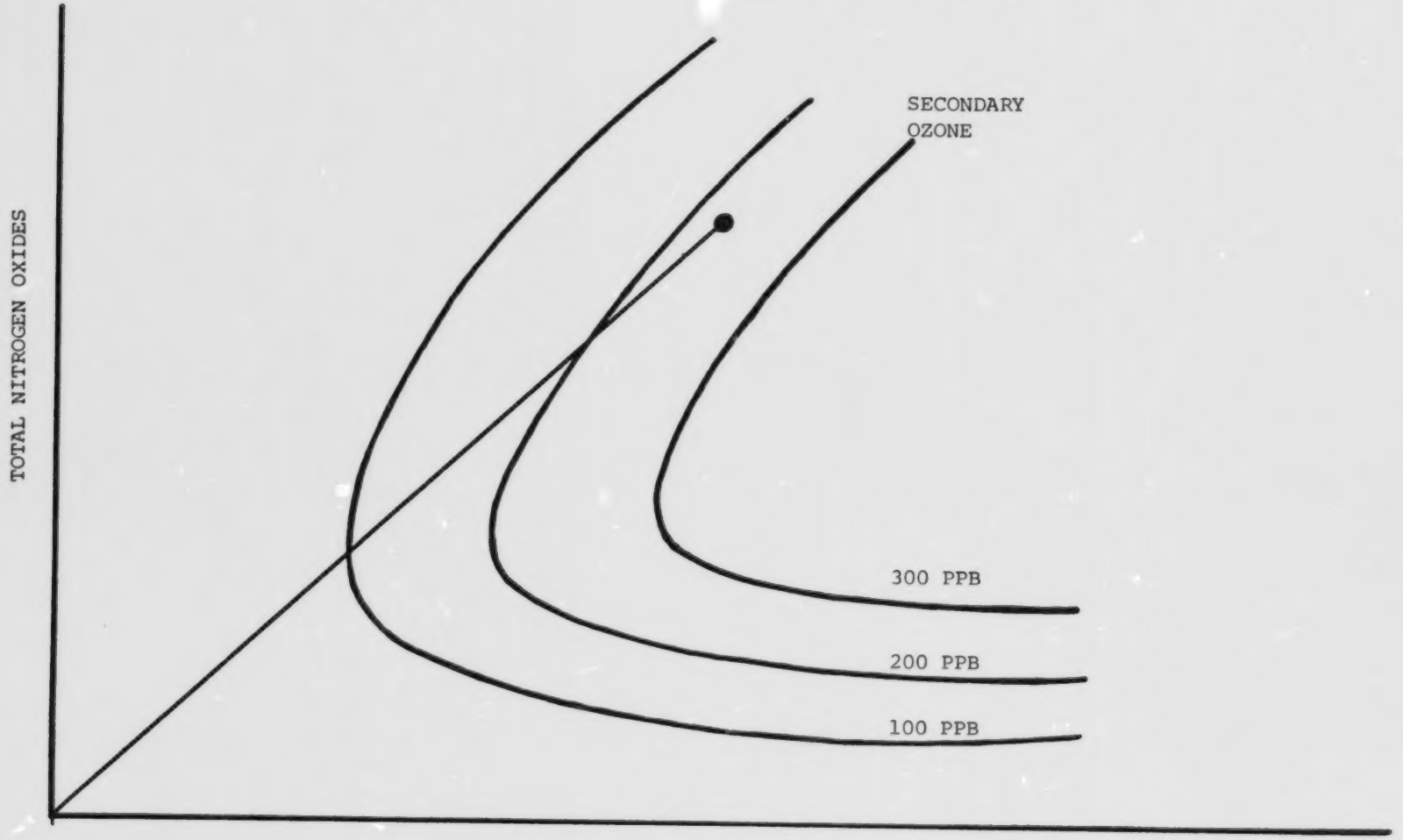

7-HOUR SEASONAL MEAN 1976-1985
SIMCOE, ONT
WHITEFACE MTN.N.Y.
HOHENPEISSENBERG, GER
OZONE CONCENTRATION (PPB)
70
60
50
40
30
20
10
0
1976
1977
1978
1979
1980
1981
1982
1983
1984
1985
YEAR

FIGURE 11

$O_3$ - $NO_x$ - NMHC RELATIONSHIP FROM EKMA MODEL (US EPA)



# MEASUREMENT OF OZONE AND OTHER OXIDANTS AT MOUNTAIN SITES IN THE EASTERN UNITED STATES

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## RÉSUMÉ

On s'est beaucoup inquiété ces derniers temps du dépérissement possible des forêts de l'est des États-Unis provoqué par les changements dans l'environnement, en particulier par l'exposition accrue des arbres à une foule d'espèces chimiques dans l'atmosphère. Un projet de recherche sur la chimie des nuages en terrain montagneux a été mis au point en vue de déterminer l'exposition des forêts de ce coin de pays à divers gaz atmosphériques et aux dépôts acides. Le choix des sites s'est porté sur ceux situés en haute altitude car ce sont derniers qui reçoivent le plus de dépôts atmosphériques et d'espèces chimiques.

Parmi les espèces chimiques d'intérêt pour la présente étude, notons les oxydants photochimiques. Ces composés peuvent être phytotoxiques et sont nécessaires à la formation de plusieurs autres espèces chimiques importantes comme l'acide nitrique et l'acide sulfurique. Le présent exposé discute donc des mesures des oxydants à deux sites forestiers de l'est des États-Unis et porte une attention particulière aux variations des concentrations avec l'altitude, aux données historiques et aux mesures à effectuer lors d'études futures.

# Measurement of Ozone and Other Oxidants at Mountains Sites in the Eastern U.S.

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## Abstract

Recently there has been a concern that forests in the Eastern United States may be in a state of decline because of changes in their environmental conditions, including an increase in their exposure to a variety of chemical species in the atmosphere. A research project, the Mountain Cloud Chemistry Project, has been initiated to determine the exposure of the forests to various atmospheric gases and acid deposition at sites in Eastern United States. Higher-altitude measurement sites have been selected at most of these locations because more forest damage has been observed at higher elevation and the exposures of forest to many chemical species and atmospheric deposition is generally greater at higher elevations.

Among the chemical species of primary interest to this study are the photochemical oxidants. These compounds can be phytotoxic and they are essential to the formation of many other chemical species of interest such as nitric and sulfuric acids. This paper discusses the measurement of oxidants at 2 of these forest sites in the Eastern United States. Observed variations of concentration with altitude, the historical measurement record, and plans for future measurements are included in this discussion.

## Introduction

In the past few years, there has been a growing concern that forests in the Eastern United States are experiencing significant unexplained dieback. Several species of trees, most notably red spruce, have exhibited decline which has been observed to be more severe at higher elevations. The Eastern Spruce-Fir Research Cooperative with the National Acid Precipitation Assessment Program has developed a comprehensive research program to deal with the changing conditions of spruce-fir forests in North America and to investigate possible causes of this unexplained forest decline.

Because of the concern about these observations in light of the severe forest dieback observed in Europe, the United States Environmental Protection Agency has initiated a study of the exposure of trees to a variety of atmospheric chemical species and acidic deposition at higher elevation sites in the Eastern United States. This project, named the Mountain Cloud Chemistry Project (MCCP), was initiated in 1984 and is presently making measurements at six sites in the Eastern U.S. (shown in Figure 1). Primarily mountain sites were chosen by MCCP because of the larger amounts of forest damage observed at higher elevation. It is hypothesized that these higher-elevation sites may have more forest damage because of their larger exposures to various atmospheric chemical species or because they experience larger amounts of acid deposition, particularly in the form of cloudwater. Among the atmospheric chemical species of primary interest are photochemical oxidants.

Figure 2 is a schematic representation of the important tropospheric reactions in which photochemical oxidants play a major role. Ozone is either brought into the troposphere by intrusions of stratospheric air or, as is most often the case with higher ozone concentrations, it is produced by the photochemical reactions of hydrocarbons and oxides of nitrogen. The photo-

dissociation of ozone initiates a chain reaction which leads to the OH radical whose tropospheric concentration is controlled by the concentration of carbon monoxide and methane and other species with which it reacts. The OH radical controls the concentrations of other important oxidizing species such as $HO_2$ and $H_2O_2$. This system of oxidant reactions controls the relative concentrations of the primary compounds emitted to the atmosphere (such as $SO_2$ or NO) and the end products (such as $H_2SO_4$ or $HNO_3$).

This paper discusses the measurement of some of these oxidants, in particular $O_3$ and $H_2O_2$, at sites in the Eastern United States. These measurements are essential to our understanding of the interaction of forests and the atmosphere both because oxidants may have direct impact on the forest and because they are essential to the homogeneous and heterogeneous processes which produce the chemical species to which the forests are exposed.

## Ozone Measurements

The longest record of ozone measurements at a rural site in North America is that of Whiteface Mt. Figure 3 is a plot of the thirteen-year record at Whiteface Mt.[1] It includes monthly averages, the monthly maximums, monthly minimums, and annual mean ozone concentrations for the years 1973 through 1985. There is no apparent trend in these values over a thirteen year period. The annual variations of ozone concentrations are readily apparent with the summer months experiencing the highest values. This seasonal variation is very similar to that predicted by the calculations of Calvert[2] and reflects the annual variation of the intensity of ultraviolet light.

Little diurnal variation is observed at the mountain sites. Figure 4 shows the average hourly ozone concentrations for Whiteface Mt. averaged over the entire thirteen-year data record. Summertime concentrations averaged 43 to 44 ppb while winter concentrations averaged 33 to 35 ppb. There is little diurnal variation in any of the seasons with average hourly concentrations varying only 2 ppb over the course of the day. This contrasts

greatly with lower level sites which exhibit a strong diurnal variation.[3] The mountain sites are generally above the nocturnal inversion and therefore do not exhibit the destruction of ozone that lower level sites experience. Figure 5 demonstrates the importance of this factor to the ozone exposure at a mountain site. Here the 1985 ozone concentration at Whiteface Mt. (altitude 1480 m) is compared to that at Huntington Forest (altitude 500 m) 35 kilometers to the south. The higher altitude "overburden" of ozone (Whiteface $O_3$ concentration minus Huntingdon $O_3$ concentration) is plotted for the year 1985. In Figure 5, the overburden is shown for the hours 6:00 A.M. to 6:00 P.M. and the hours 6:00 P.M. to 6:00 A.M. During both day and night, during most of the year there are substantially higher $O_3$ concentrations measured at the higher elevation sites. This is indicative of the altitude gradient of ozone concentration observed in rural areas with higher concentrations aloft and destruction at the surface. This gradient is enhanced during the nocturnal inversion because the inversion isolates the lower level site from the ozone reservoir aloft. This accounts for the larger overburden at night.

## Hydrogen Peroxide

Hydrogen peroxide is a particularly important oxidizing species to the study of the impact of chemical species in the atmosphere on the vegetation at higher elevation sites. The presence of hydrogen peroxide in cloudwater resting on leaves has been shown to cause stress to plants.[4] Hydrogen peroxide has also been shown to be the most important oxidant in cloudwater because it oxidizes $SO_2$ to sulfate with an acid catalytized reaction whose rate is not reduced as pH increases.[5] Recently, Kok[6] has developed a continuous gas phase $H_2O_2$ monitor and $H_2O_2$ is now being monitored at the MCCP sites. Whiteface Mt. has been making continuous atmospheric $H_2O_2$ measurements since June 1986 and has measured $H_2O_2$ in cloudwater since 1983.[7]

An example of these measurements at Whiteface Mt. is shown in Figure 6. The histogram shows that summertime hourly average concentrations of $H_2O_2$ at Whiteface range from 0.4 to 2.6 ppb with the most common values

measured in the range of 0.2 to 0.8 ppb. During the winter, concentrations of $H_2O_2$ are below the minimum detectable level of 0.1 ppb. There is no apparent diurnal variation in $H_2O_2$ concentrations. Similar data is shown in Figures 7 and 8 for Whitetop Mt., Virginia. The summertime $H_2O_2$ concentrations (Figure 7) range from less than the minimum detectable level to 2.6 ppb with the largest portion of the measurements between 0.2 and 1.6 ppb. The fall measurements at Whitetop, Virginia show much lower concentrations with all measurements less than 0.6 and the bulk of the measurements less than the minimum detectable level.

It is evident that during the winter months much less $H_2O_2$ is formed. This is due both to the lower amounts of uv light that is present and the colder temperatures. The lack of $H_2O_2$ present during the colder months causes much less oxidation of $SO_2$ and $NO_2$ to take place in cloudwater and thus heterogeneous oxidation reactions are of minimum importance during this period.

Future Objectives of Measurement Program

Elevated ozone concentrations are often an indicator of an elevated oxidation capacity of the atmosphere both because ozone itself is an oxidant and because ozone is often accompanied by a variety of other oxidants including $H_2O_2$, OH and other free radicals, periacetyl nitrate and a variety of organic oxidants. It is plausible that some of the vegetation damage attributed to ozone may be due to the presence of these compounds, many of which are not routinely measured. Measurement of these chemical species is of interest to understanding not only the chemistry of the troposphere but also to understanding the mechanisms by which air pollutants may cause forest stress.

In light of the need for technology to measure these more exotic chemical species, a Center for Instrumentation and Technology was included in the Mountain Cloud Chemistry management plan. The Center has developed a mobile laboratory which is capable of traveling to remote sites to make measurements of a wide variety of chemical species.

The most versatile piece of instrumentation included in the mobile laboratory is a tunable diode laser system.[8] This instrument operates on the principle of infrared absorption using laser radiation at narrowly defined wavelengths. A wide variety of chemical species can be measured by this technique with a minimum detectable level of 0.2 ppb. Present capabilities include $SO_2$, $NO_2$, NO, $H_2O_2$, HCO, $HNO_3$, and $NH_3$. Developmental work will be conducted to measure PAN and free radicals.

The mobile laboratory also contains a $H_2O_2$ monitor and a high-sensitivity chemiluminescent NO monitor. This system will greatly expand the measurement capabilities of the program and will improve our ability to understand the mechanisms by which these species are formed and their potential to impact the forest environment.

## Summary

Measurement of photochemical oxidants and understanding the mechanisms by which they react with other species is essential to the study of the forest's exposure to atmospheric pollutants and acid deposition. The MCCP measurement program now underway, together with new programs planned for the next few years, promise to greatly increase our knowledge of these complex chemical species and their impact on the forest ecosystem.

## Acknowledgement

The Mountain Cloud Chemistry Project is supported by the U.S. Environmental Protection Agency (sponsor no. CR812254020). The $H_2O_2$ measurements at Whiteface Mt. were supported by the Empire State Electric Energy Research Corporation (contract no. 8210). Ozone measurements at Whiteface Mt. and Huntington forest are conducted by the New York State Department of Environmental Conservation, Division of Air Resources' Continuous Air Monitoring Section. The MCCP Mobile Lab was developed with funds from the New York State Energy Research and Development Authority (contract no. 818-EIM-CE-86). Thanks to Stephanie Liddle for her careful typing of the manuscript and to Gary Lanphear and Carol Clas for drafting the

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8) Schiff, H.I., Hastie, D.R., Makay, G.I., Iguchi, T., and B.A. Ridley, 1983: Tunable diode laser systems for measuring trace gases in tropospheric air. Environ. Sci. and Technol., 17, 352A-364A.

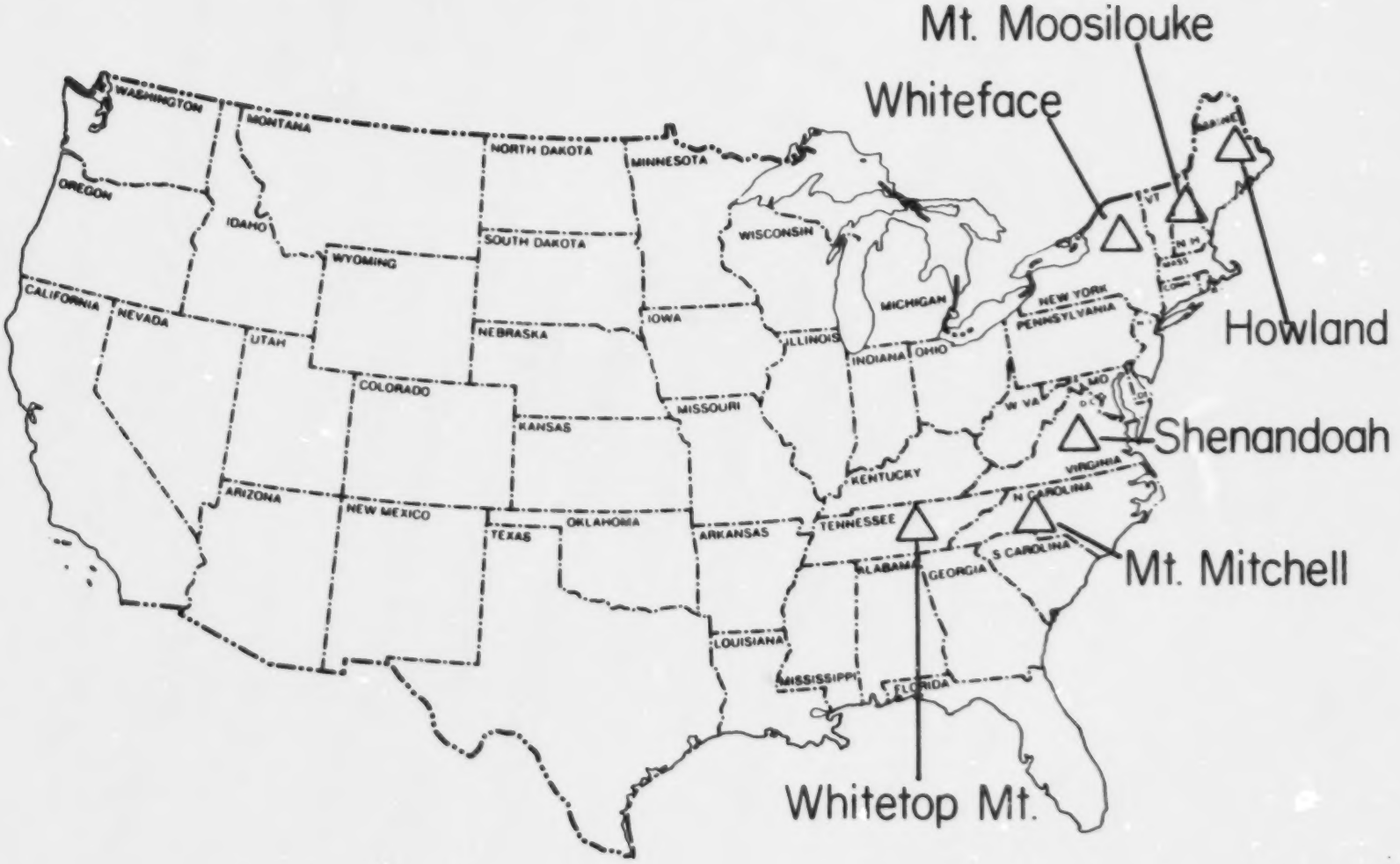


Figure 1 Mountain Cloud Chemistry Measurement Sites

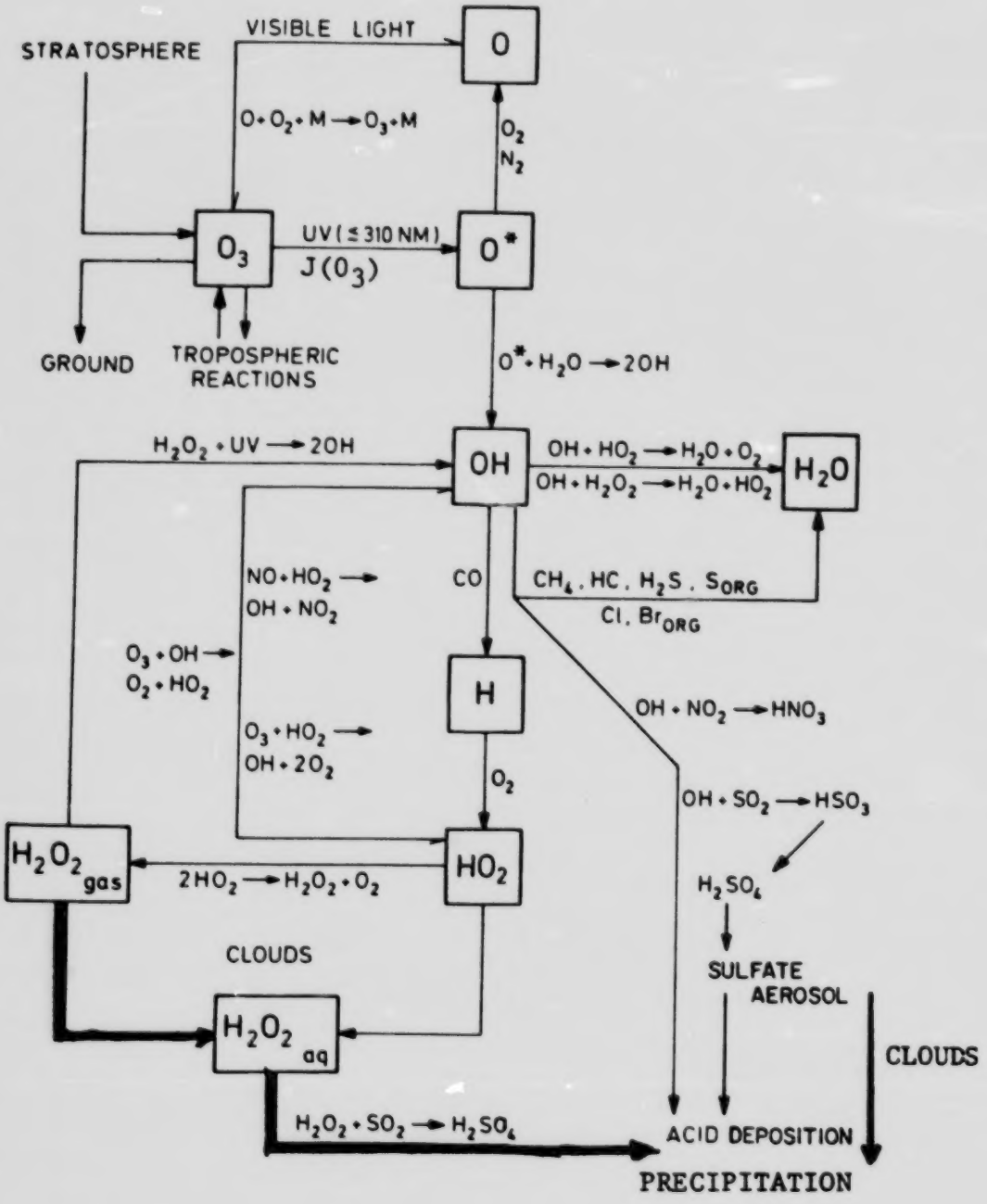


Figure 2 Schematic representation of some important homogeneous atmospheric reactions.

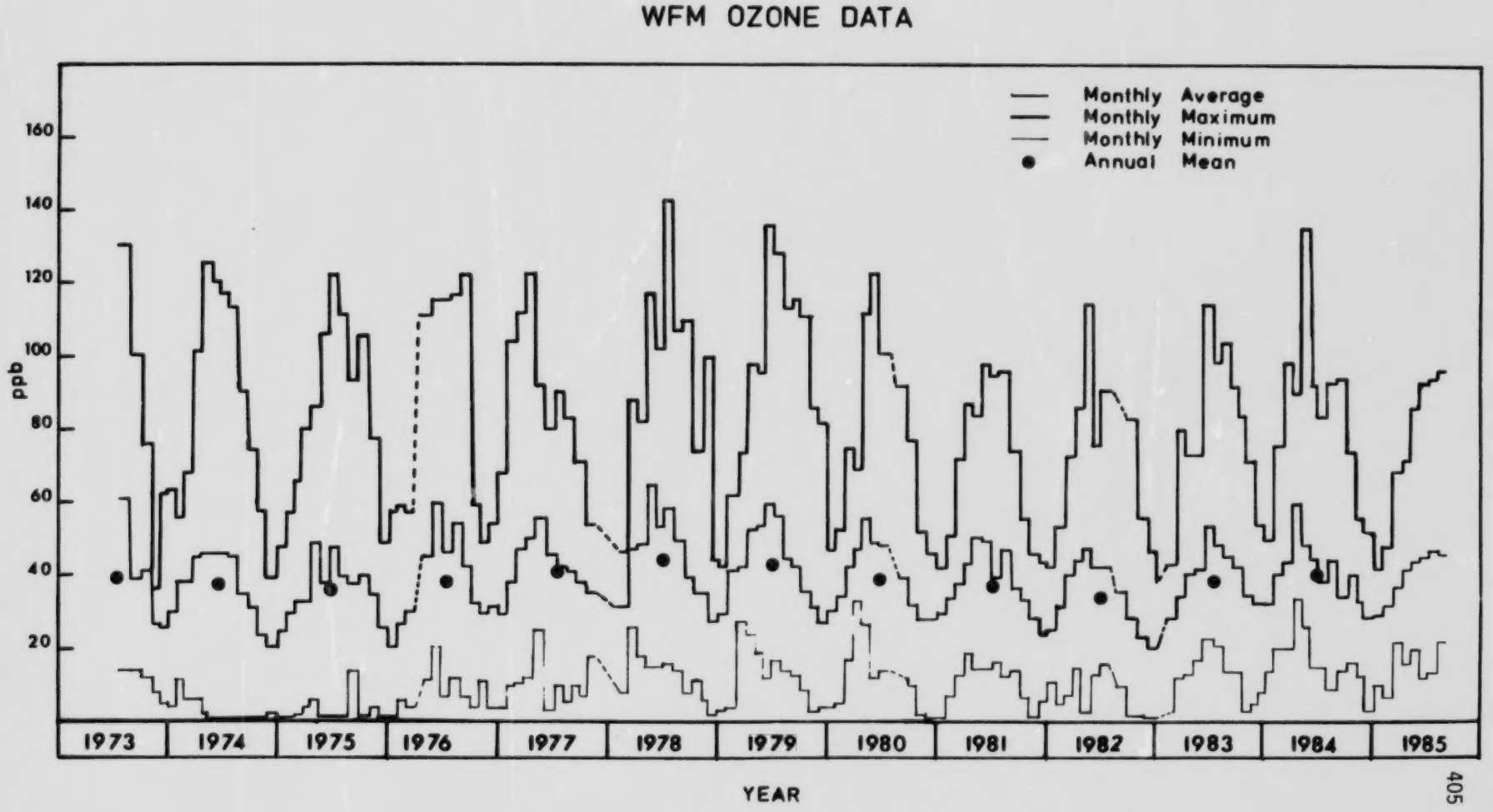
WFM OZONE DATA
Monthly Average
Monthly Maximum
Monthly Minimum
Annual Mean
160
140
120
100
80
60
40
20
ppb
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
1984
1985
YEAR
405

Figure 3

# WHITEFACE MT OZONE HOURLY AVERAGES (AUG 1973 - DEC 1985)

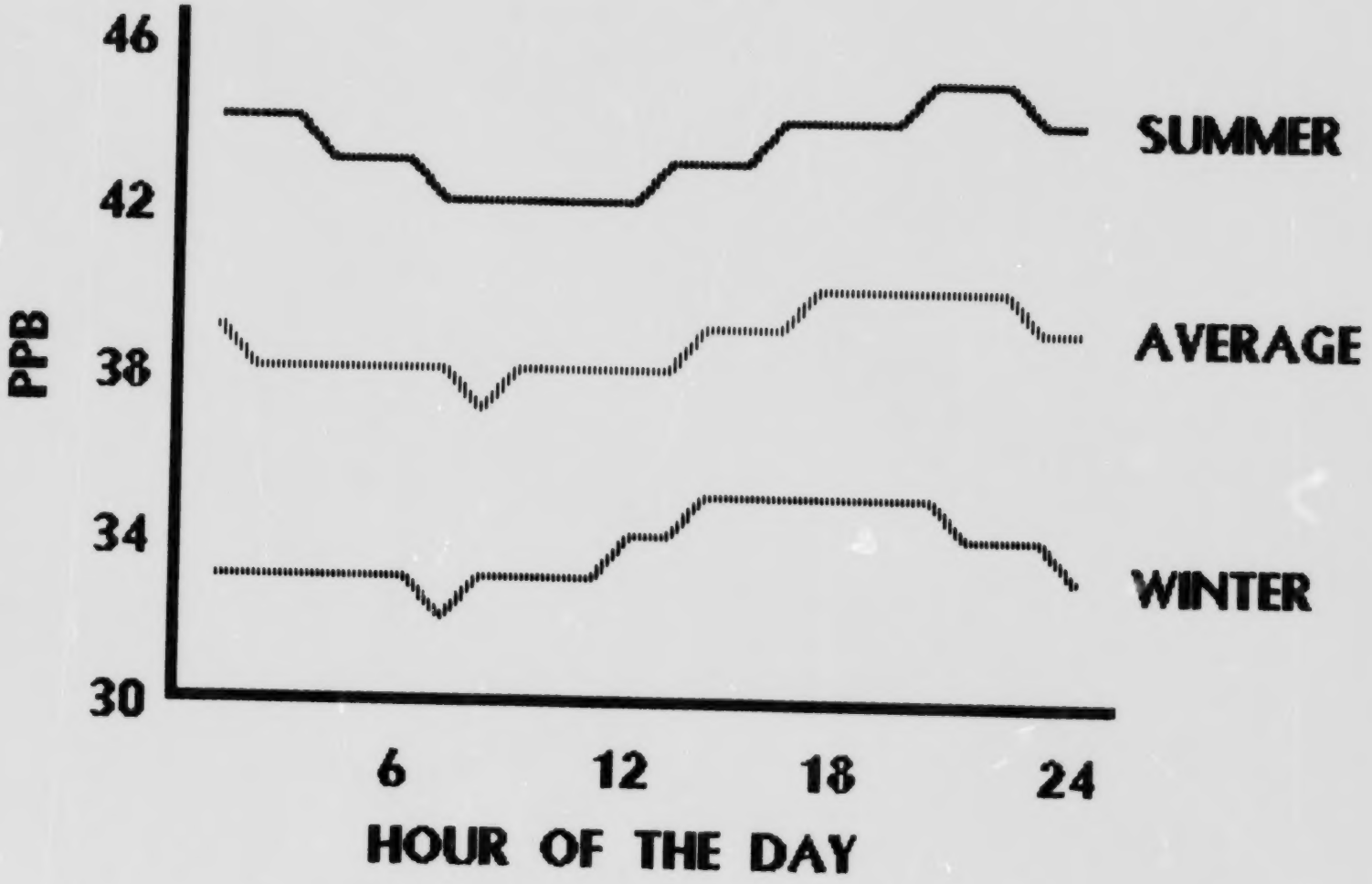


Figure 4

# OZONE ALTITUDE GRADIENT

## WHITEFACE MT VS HUNTINGTON FOREST 1985

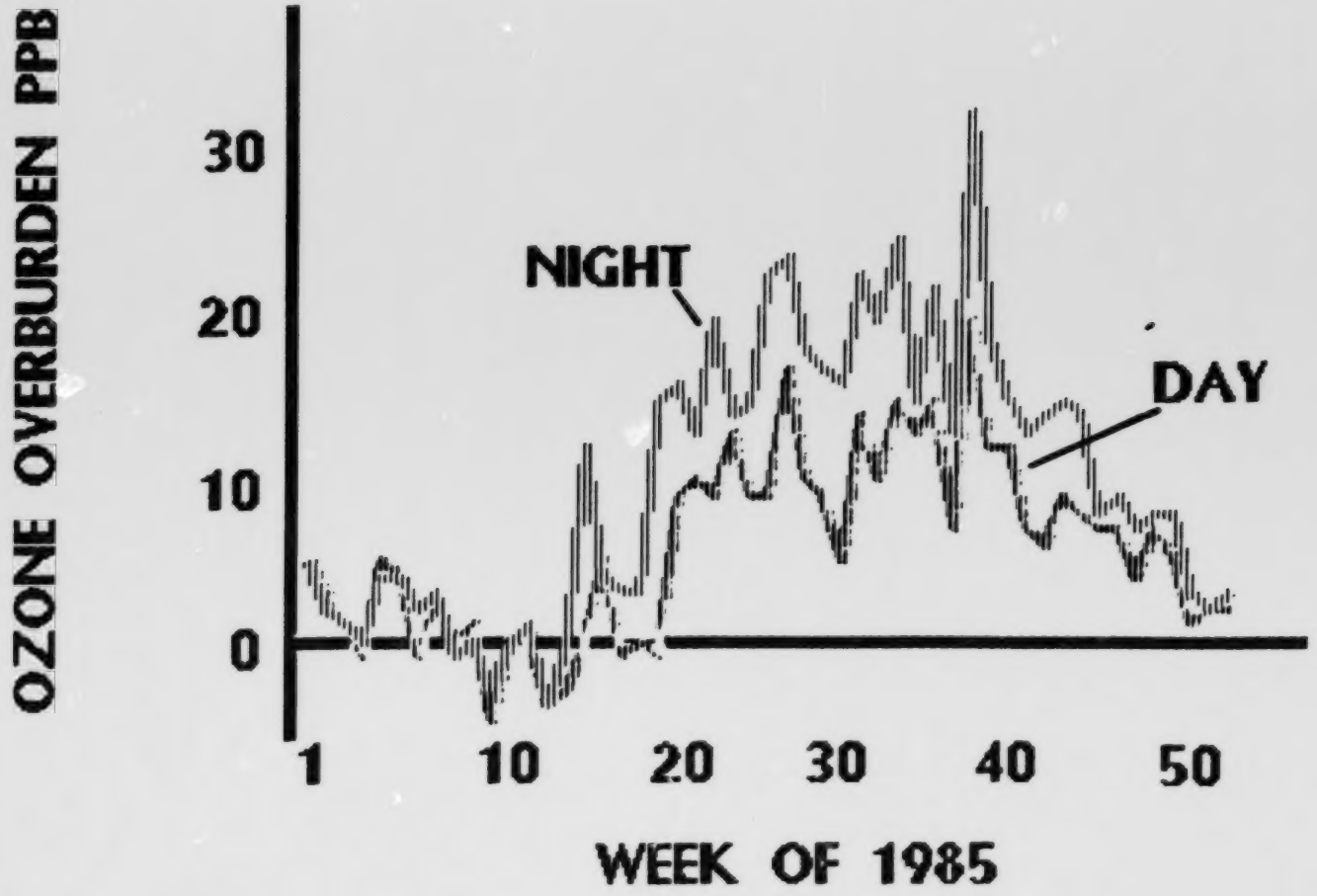


Figure 5

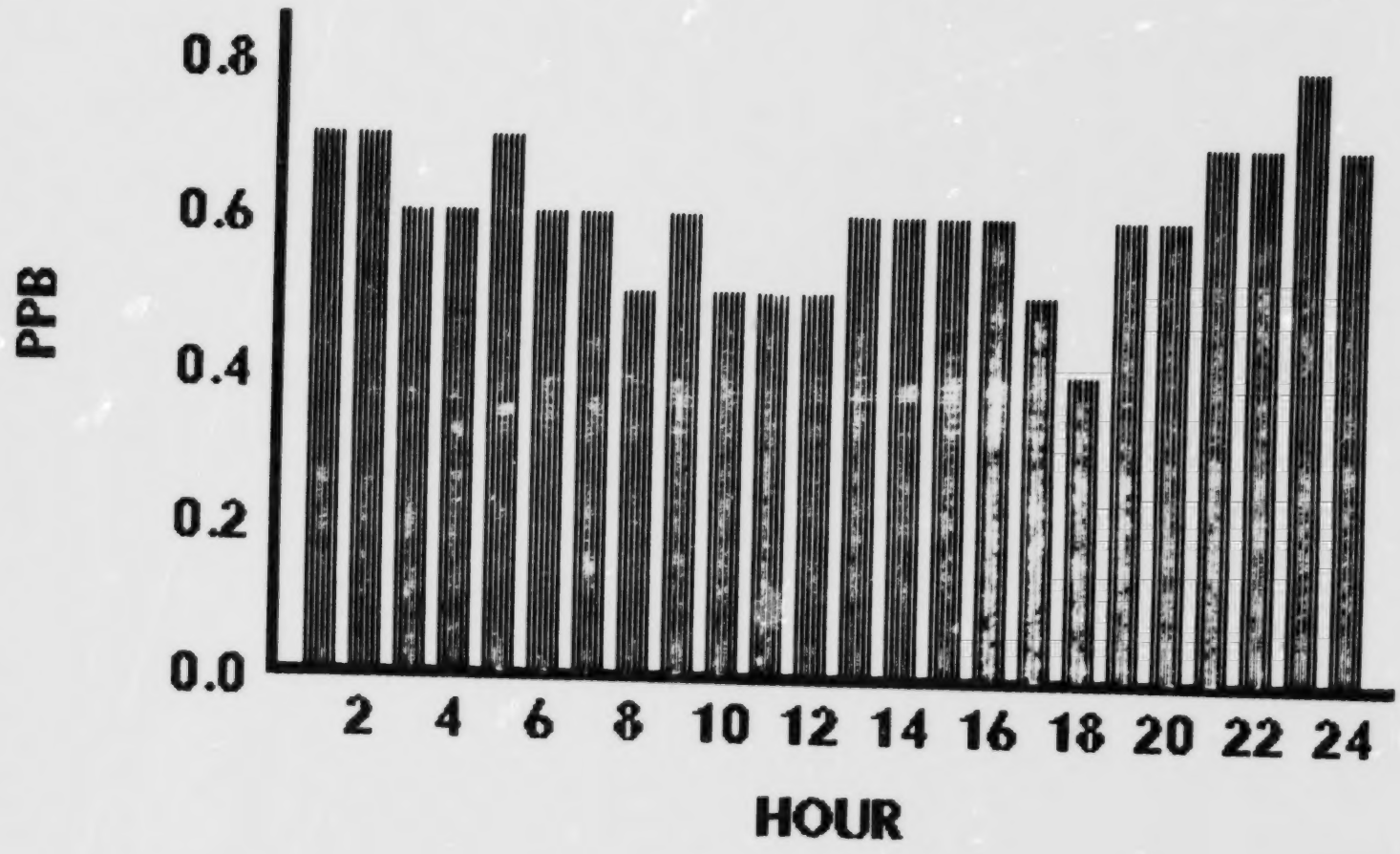
GAS PHASE HYDROGEN PEROXIDE
WHITEFACE MT SUMMER 1986
PPB
0.8
0.6
0.4
0.2
0.0
2
4
6
8
10
12
14
16
18
20
22
24
HOUR

Figure 6

# WHITETOP GAS PHASE HYDROGEN PEROXIDE

## SUMMER 1986

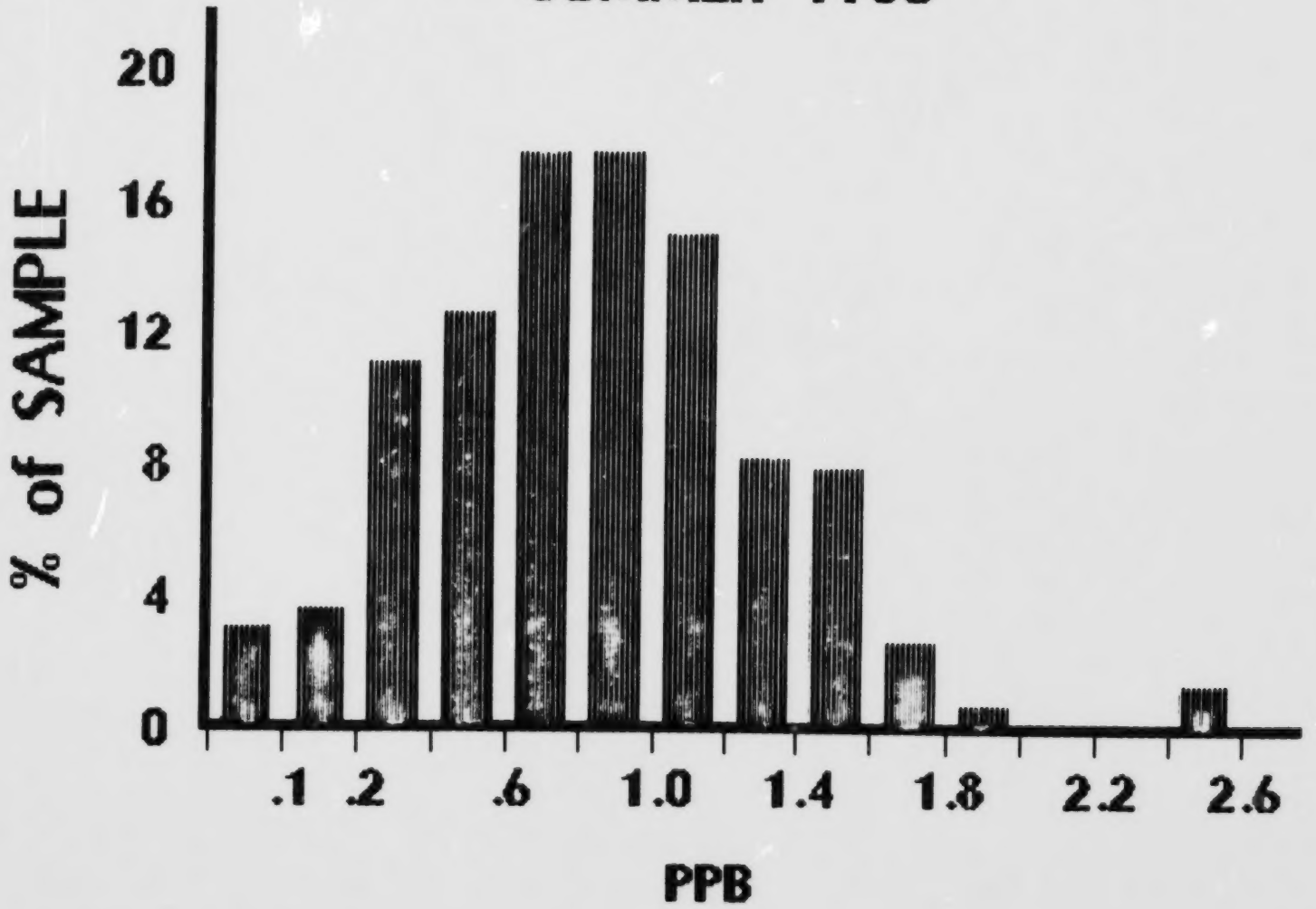


Figure 7

# WHITETOP GAS PHASE HYDROGEN PEROXIDE

## FALL 1986

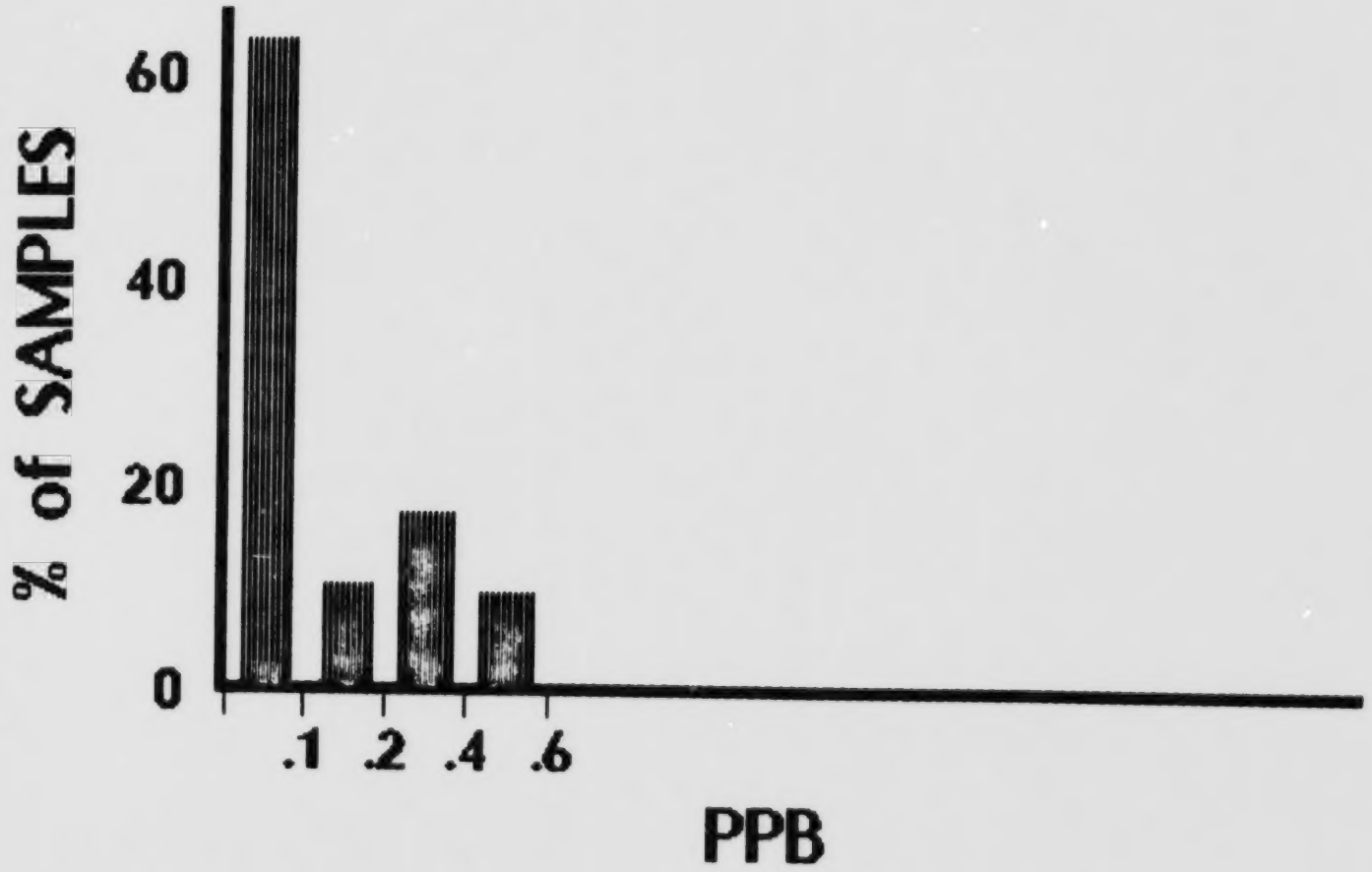


Figure 8

# GEOGRAPHIC VARIATIONS OF OZONE CONCENTRATIONS AT HIGH AND LOW ELEVATION RURAL SITES IN QUÉBEC

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## RÉSUMÉ

Les données sur l'ozone présentées dans le présent exposé ont été relevées de mai à septembre 1986 dans trois sites en haute altitude (845, 860 et 970 m) et dans une vallée (250 m) du sud du Québec. Les pourcentages saisonniers des concentrations horaires supérieures à 50 parties par milliard (ppb) sont respectivement de 20,0 pour cent, 13,7 pour cent et 6,5 pour cent aux monts Roundtop (RT), Tremblant (MT) et Montmorency (MO), les trois sites montagneux. Le pourcentage maximum d'heures dépassant 50 ppb a été de 30,7 pour cent en mai à RT. Les pourcentages saisonniers d'heures à concentrations plus fortes que 80 ppb sont respectivement de 0,8 pour cent, 0,3 pour cent et 0,3 pour cent à RT, MT et MO. Le pourcentage le plus élevé d'heures dépassant 80 ppb a été de 2,2 pour cent en juin à RT. Dans la vallée Roundtop (RV) seulement 2,9 pour cent des heures ont eu des concentrations supérieures à 50 ppb et aucune n'a dépassé 80 ppb. Les concentrations saisonnières moyennes d'$O_3$ sont de 40,0 ppb à RT, 33,7 ppb à MT, 20,5 ppb à MO et 22,6 ppb à RV. La plus forte moyenne hebdomadaire de 44,5 ppb a été enregistrée en mai à RT. La concentration maximale d'$O_3$ pour 15 minutes est de 95,4 ppb en juillet à MO.

Il existe une uniformité régionale dans les épisodes d'$O_3$ se produisant dans le sud du Québec, par contre la durée moyenne de ces épisodes et l'ampleur moyenne des concentrations diminuent du sud au nord. Il existe aussi une forte gradation verticale dans les concentrations d'$O_3$ et dans la durée des épisodes pour les forêts en altitude recevant de fortes doses d'$O_3$. Les plus fortes concentrations d'$O_3$ aux sites montagneux se produisent souvent en fin de soirée de sorte que les effets sur la santé des forêts dans de telles circonstances devraient faire l'objet d'études.

# Geographic Variation of Ozone Concentrations at High and Low Elevation Rural Sites in Québec

by

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Abstract

Ozone data are presented here for three high elevation sites (845, 860 and 970 m) and one valley site (250 m) in southern Québec for the period May to September 1986. The seasonal percentage of observation hours with concentrations > 50 ppb were 20.0%, 13.7% and 6.5% at the three mountain sites Roundtop Mtn. (RT), Mt. Tremblant (MT) and Montmorency (MO) respectively. The maximum percentage of hours > 50 ppb was in May at RT, 30.7%. The seasonal percentages of hours with concentrations > 80 ppb were 0.8%, 0.3% and 0.3% at RT, MT and MO respectively. The highest percentage of hours > 80 ppb was in June at RT, 2.2%. The Roundtop valley site had only 2.9% of the hours with concentrations> 50 ppb and no hours with concentrations > 80 ppb. The seasonal mean $O_3$ concentrations were 40.0 ppb at RT, 33.7 ppb at MT, 29.5 ppb at MO and 22.6 ppb at RV. The highest monthly mean was 44.5 ppb recorded in May at RT. The highest monthly mean was 44.5 ppb recorded in May at RT. The maximum 15 min $O_3$ concentration was 95.4 ppb at MO in July.

There is a regional uniformity in the occurrence of $O_3$ episodes in southern Québec but the mean duration of the episodes and the mean magnitude of the concentrations decreases as one moves from south to north. There is a strong vertical gradient in $O_3$ concentrations and event durations with higher elevation forests receiving higher $O_3$ dosages. The highest $O_3$ concentrations at the mountain sites often occur in late evening and the effects of this on forest health should be explored.

## 1. Introduction

There is considerable interest at the moment in the possible role of ozone in the observed forest declines in Europe and North America. Hinrichsen (1986) has reviewed six schools of thought on the role of air pollutants in forest declines and has ranked them in order of priority. In North America, in low elevation forests, he ranks ozone first. In high elevation forests he would rank it third behind nitrogen saturation and heavy metal fallout. Hinrichsen also ranks ozone first in western Europe and second in eastern Europe. Linzon (1986) also concludes that ozone is the most prevalent phytotoxic air pollutant on a regional scale in eastern North America. Haughs and Wright (1986) propose that the regional patterns of forest dieback in Europe can be explained based on a combination of a predisposing factor such as soil acidification and an inciting factor such as ozone damage. Lefohn and Mohnen (1986) have presented the ozone data for a number of sites in the Federal Republic of West Germany and for Whiteface Mountain, New York. The data vary considerably from site to site and clearly show the low frequency of acute events (> 80 ppb or > 100 ppb). Other authors, e.g. McLaughlin et al., (1982), Williams and Williams, (1986), have pointed out the important effects on trees resulting from short term exposures to high concentrations of ozone.

No high elevation ozone data for southeastern Canada has been available to date and data for rural low elevation sites in forested areas is very sparse. Chung (1977) investigated the role of regional transport in the determination of ozone concentrations in southern Ontario. Linzon et al. (1984) summarize growing season data for Dorset, Ontario for an 8-year period. Mukammal et al. (1985) prepared an ozone climatology for southern Ontario for a 4-year period including urban and rural sites. Anlauf et al. (1975, 1980, 1985) have measured the concentration of ozone and other gaseous species at urban and rural sites in southern Ontario. Kelly et al. (1986) report summer 1981 ozone data for some rural agricultural sites near Windsor, Ontario. Data are conspicuously lacking from southern Québec where dieback of hardwood forests, particularly sugar maple, has been well documented (Québec Ministry of Energy and Resources, Map 1985).

Schemenauer (1986) and Schemenauer et al. (1986) have described the initiation and first measurements from the Chemistry of High Elevation Fog (CHEF) program in southern Québec. CHEF is designed to provide meteorological and air chemistry measurements in support of forest effects studies in southeastern Canada. It is closely tied to the Mountain Cloud Chemistry project (MMCP) in the U.S. CHEF is providing measurement of vertical variations of meteorological parameters, cloud water and precipitation chemistry, and gaseous pollutant concentrations at two sites (three in 1986) on a daily basis. The ozone data from three rural, forested, high elevation (845-970 m) sites and one low elevation (250 m) site for the period May to September 1986 are presented in this paper.

## 2. Instrumentation and measurement protocol

TECO 49 u.v. photometric ozone analyzers with automatic pressure and temperature compensation were used for measurement of ambient ozone concentrations. Calibrations using sources traceable to NBS standards were conducted at the beginning and end of the field measurements for each analyzer. On-site operators carried out routine diagnostic and zero checks.

The continuous ozone measurements were averaged for 15 min to conform to the sample period used for the meteorological data. The ozone analyzer inlets at the three high elevation sites, Roundtop Mtn. (RT) 845 m, Mt. Tremblant (MT) 860 m, and Montmorency (MO) 970 m, (see Schemenauer, 1986 for site descriptions) are all on rooftop platforms about 2 m above the tops of the nearest trees. The inlet at the Roundtop valley (RV) site (250 m) is on the side of a small building about 2 m above a grass surface. All inlets lines were filtered to remove particulates. The locations of the sites are as follows: RT 45°05'19"N 72°33'25"W, southeast of Montreal; MT 46°12'50"N 74°33'20"W, northwest of Montreal; MO 47°19'15"N 71°10'28"W; north of Québec City; and RV 45°04'34"N 72°42'05"W, southeast of Montreal.

The number of hours per day or per month with ozone concentrations $\geq$ 50 ppb or $>$ 80 ppb were calculated by first correcting for the instrument's zero offset and then totalling the number of 15-min periods and dividing

by 4. The monthly mean ozone concentrations represent the mean 15-min sample concentrations. Growing season averages were calculated for the period May to September.

3. Peak ozone concentrations (May - September, 1986)

Figures 1 and 2 show the number of hours per day that $O_3$ concentrations exceeded 50 and 80 ppb respectively at the Roundtop Mtn. site. Figures 3 and 4 show similar data for Mt. Tremblant and Figures 5 and 6 for Montmorency. Figure 7 gives the number of hours per day that $O_3$ concentrations were $>$ 50 ppb at the Roundtop valley site. Concentrations never exceeded 80 ppb in the valley during the measurement period.

The data in the figures clearly show the episodic nature of the high ozone events. Periods with concentrations $>$ 50 ppb typically last 3 or 4 days with similar spacing between events. On four occasions at RT and one each at MT and MO, the $O_3$ concentrations were $>$ 50 ppb for a full 24 h. Days when the $O_3$ concentrations exceeded 50 ppb were frequent in each month with the exception of September.

Days with $O_3$ concentrations $>$ 80 ppb were infrequent at the mountain sites and nonexistent at the valley site. One event is of particular interest, though, because it was observed at all 3 mountain sites on 24 and 25 July. It seemed to appear first at RT with concentrations exceeding 50 ppb (but $<$ 80 ppb) on 23 July, then exceeding 80 ppb for 4.75 h on 24 July and 0.25 h on 25 July, and finally falling to concentrations $<$ 80 but $>$ 50 ppb on 26 July. At MT the high concentrations were part of a 5-day event with concentrations $>$ 80 ppb for 0.5 h on 24 July and 7 h on 25 July. At MO the event was also 5 days long with concentrations $>$ 80 ppb for 1 h on 24 July and 5.75 h on 25 July. The measured site winds during the $>$ 80 ppb $O_3$ episode were 250°-265° at RT, 265°-290° at MT and 270°-280° at MO. Allowing for some differences due to site topography, there is good agreement in that all sites experienced consistent westerly winds over the 2-day episode of $>$ 80 ppb $O_3$. The days were warm and sunny with warm nights. The highest $O_3$ value at RT,

91.8 ppb, occurred at 2215 EST on 24 July. A peak value of 89.5 ppb at 1245 EST on 25 July was measured at MT, and a peak of 95.4 ppb at 1700 EST on 25 July at MO. Winds were unusually strong at the 3 sites, approximately 7.5 m $s^{-1}$ at RT, 11.5 m $s^{-1}$ at MT and 11 m $s^{-1}$ at MO. The observations were consistent with the synoptic situation which showed a high pressure system moving eastward from western New York to a position off Cape Cod during this period. The return flow around the high was from the southwest turning more westerly at the northern sites. The observations are consistent with earlier observations of high $O_3$ concentrations being associated with slowly moving high pressure systems, e.g. Mukammal et al. (1985) and Kelly et al. (1986). The somewhat stronger winds measured in the present case are due to the 3 sites being well removed from the center of high pressure.

Table 1 gives the percentage of observation hours at each site in each month with concentrations > 50 ppb. The highest percentages at RT and MT were in May, 30.7% and 21.3% respectively. The next highest month was August with values of 22.2% at RT, 16.1% at MT and 8.9% at MO. The Roundtop valley (RV) site had its highest percentage (3.8%) of observations > 50 ppb in August. (No May measurements were made at RV.) The seasonal average percentage of $O_3$ concentrations with values > 50 ppb decreases markedly from south to north (Figure 9): 20.0% at RT, 13.7% at MT and 6.5% at MO. There is also a very large decrease with altitude, from to 20.0% at RT (845 m) to 2.9 at RV (250 m).

It is important to document the duration of high $O_3$ events. The daily durations are shown in the figures and the monthly and seasonal mean values are given in Table 2. On days with $O_3$ concentrations > 50 ppb the seasonal mean daily durations are 9.1 h at Rt, 7.9 h at MT and 5.7 h at MO. Again there is a south to north decrease in the severity of the $O_3$ episodes. The mean seasonal duration at RV was 3.9 h, only 43% of the mean duration at the corresponding mountain site.

Table 3 summarizes the percentages of observation hours with $O_3$ concentrations > 80 ppb for each month and for the season. The southernmost site, RT,

had a seasonal mean of 0.8%, MT 0.3% and MO 0.3%. Monthly values were as high as 2.2% at RT in June. Months with no concentrations > 80 ppb were frequent but only at the low elevation valley site, RV, were they totally absent. Mean daily event durations were not calculated for each month since the number of occurrences was so small.

Though the Roundtop Mtn. valley site at 250 m showed a clear diurnal cycle in $O_3$ concentrations with afternoon maxima and early morning minima, this was not the case at the Roundtop Mtn. ridge site at 845 m. Figure 8 shows the $O_3$ concentrations for a 5.5-day period starting at noon (NO) on 28 June 1986. The concentrations at the two sites agreed quite well at mid-day when the boundary layer was well mixed. However, differences during the night can be large as is well illustrated on days 183 and 184. In the early morning of day 184 the valley concentrations drop to about 10 ppb as $O_3$ is deposited, or destroyed by NO present in the lower boundary layer. Meanwhile the ridge $O_3$ concentrations rise to about 50 ppb. Since this $O_3$ is not being produced in the absence of sunlight it must be advected into the measuring site. Potential sources are the upper part of the planetary boundary layer where $O_3$ sinks may not be so evident, from the free troposphere which is a large reservoir of $O_3$ or from higher altitudes over urban areas as Zellner and Moussiopoulos (1986) discuss. Whatever the origin, high nocturnal $O_3$ concentrations may have important consequences for tree health in some species since processes involved in growth respiration such as the degree of opening of the stomates may make trees more responsive to oxidant damage at certain times of the day.

4. Mean ozone concentrations

a. High elevation sites

The monthly and seasonal (growing season) mean $O_3$ concentrations for each site are given in Table 4. The maximum 15-min value is also given for each month. The pattern is similar to that seen for the peak values in Table 3. Of the three high elevation sites, RT had the highest seasonal mean (40.0 ppb), followed by MT (33.7 ppb) and MO (29.5 ppb). The Montmorency seasonal mean is the lowest at least in part due to the fact that data were not

available for the month of May. This is the month with the highest mean $O_3$ concentrations at RT (44.5 ppb) and MT (40.7 ppb). However, even adjusting for the lack of data for May at MO, this site would still have a slightly lower seasonal mean $O_3$ concentration than MT and a mean perhaps 25% lower than at RT.

The maximum 15-min concentrations measured each month are not closely linked to the monthly mean values. The highest monthly maximum was 95.4 ppb recorded in July at MO. The lowest monthly maximum was 59.5 ppb in September at MO. When dealing with events as extreme as the highest 15-min value in a month, one presumably can expect variability to be introduced by local topographically induced wind flows and the effects this might have on regional and local sources and sinks of $O_3$.

The trend at all three high elevation sites is for the monthly mean $O_3$ concentrations to decrease from May to June to July and then to increase in August before falling sharply in September. The tendency for high $O_3$ concentrations to occur early in the summer followed by a rapid drop in late summer is consistent with trends reported worldwide. The concurrent month to month changes seen here at the three sites are presumably peculiar to the synoptic patterns experienced in 1986. The observation of the consistency of this data on a regional scale is important. The three sites form a triangle with sides over 200 km long. Forests growing at higher elevations over this very large area of southern Québec will experience similar trends in mean and peak concentrations with only the magnitudes decreasing as one moves northwest from RT to MT of northeast from RT to MO.

b. Low elevation site

The seasonal mean value at RV (22.6 ppb) is considerably lower than that measured at RT (40.0 ppb). The individual monthly means are also lower as are the maximum monthly concentrations. Considering that it is only low elevation rural data that is available in the literature (e.g. Linzon et al. 1984; Mukammel et al. 1985; Anlauf et al. 1975, 1980, 1985) this is an impor-

tant finding. All forests in southern Québec are not found between sea level and 250 m. Considerable forested areas exist at elevations up to about 1000 m. These forests will be exposed to higher $O_3$ concentrations and longer periods of high concentrations than will the more extensively studied forests in lowland areas.

## 5. Discussion

The data presented here for southern Québec demonstrate that ozone concentrations at elevations of 845-970 m show a markedly uniform response to changing weather patterns on a scale of approximately 30,000 $km^2$. Major episodes generally occur on the same days at the 3 sites. There is, however, a decrease in both monthly and seasonal mean $O_3$ concentrations as well as the duration of high concentration events as one moves northwest and northeast from Roundtop Mtn. The highest monthly mean $O_3$ concentration was 44.5 ppb at RT in May, the maximum 15-min concentration was 95.4 ppb at MO in July and the day with the greatest number of hours (9) with concentrations > 80 ppb was at RT in June. The seasonal (May-Sept.) mean $O_3$ concentrations were 40.0 at RT, 33.7 at MT and 29.5 at MO.

Even though the ozone data from the 1986 growing season does not suggest that acute (Hibben, 1969) damage may have occurred at the three high elevation sites, two points must be borne in mind. First, the responses of the full range of coniferous and deciduous tree species to ozone while growing in realistic environmental conditions are poorly understood. This is particularly true of the responses of trees to long term moderately high mean ozone concentrations, a point that Roberts (1984) has emphasized. Reich et al. (1983) show that some lowering of the rates of net photosynthesis in sugar maple seedlings can be obtained with the values and durations of exposure to ozone observed here. Second, whereas occurrences of ozone concentrations > 50 ppb are periodic and associated with the changing synoptic pattern, the extreme events with concentrations > 80 ppb are relatively rare, averaging 0.8% of the observation time at Roundtop Mountain. Therefore, one will have to look at a longer data base to determine if ozone concentrations capable of inducing acute foliar damage are occurring at the sites. Certainly the data

of Lefohn and Mohnen (1986) for Whiteface Mountain, 135 km southwest of Roundtop Mountain, show a marked year-to-year variation in maximum ozone concentrations.

The data presented here show a strong vertical gradient in ozone concentrations in rural Québec. The higher elevation (845 m) site at Roundtop has much higher monthly mean and seasonal concentrations as well as more high ozone episodes with longer durations than does the valley site (250 m). Gagnon et al. (1986) have demonstrated that the severity of damage to sugar maples and other hardwood tree species increases with altitude. This may be due entirely to poor soils and/or harsh climatic conditions, but the enhanced rates of acidic deposition (Schemenauer, 1986) and increased exposure to gaseous pollutants may play a role. It is important to bear in mind that pollutants other than $O_3$ may also have strong vertical gradients. At the moment there is no demonstrable physical linkage between the observed ozone concentrations and hardwood or coniferous forest damage at the mountain sites. This will be addressed during the 1987 growing season by carefully documenting the health of the forest at both Roundtop Mtn. and Mt. Tremblant with particular emphasis on an examination of foliage after each occurrence of ozone concentrations > 80 ppb.

A final point should be made. The data from the three high elevation sites often show maximum $O_3$ concentrations near midnight. An example is given in Figure 8. This suggests that if trees are being damaged by $O_3$ it is important for the forest effects community to examine the potential damage from high nocturnal as well as high daytime episodes.

Acknowledgements

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| | May | June | July | August | September | Season |
|---|---|---|---|---|---|---|
| Roundtop ridge | 30.7 | 19.0 | 17.6 | 22.2 | 12.4 | 20.0 |
| Roundtop valley | - | 0 | 2.1 | 3.8 | 2.7 | 2.9 |
| Mt. Tremblant ridge | 21.3 | 12.9 | 14.9 | 16.1 | 4.6 | 13.7 |
| Montmorency summit | - | 8.7 | 7.4 | 8.9 | 1.2 | 6.5 |

Table 1. Percentage of observation hours with ozone concentrations > 50 ppb.

| | May | June | July | August | September | Season |
|---|---|---|---|---|---|---|
| Roundtop ridge | 11.2 | 8.6 | 6.2 | 10.3 | 11.1 | 9.1 |
| Rountop valley | - | 0 | 2.9 | 4.0 | 5.5 | 3.9 |
| Mt. Tremblant ridge | 8.6 | 7.2 | 7.9 | 8.5 | 6.6 | 7.9 |
| Montmorency summit | - | 6.6 | 6.1 | 5.5 | 3.5 | 5.7 |

Table 2. Mean daily duration (in hours) of ozone concentrations > 50 ppb on days when concentrations exceed 50 ppb.

| | May | June | July | August | September | Season |
|---|---|---|---|---|---|---|
| Roundtop ridge | 0.7 | 2.2 | 1.1 | 0 | 0 | 0.8 |
| Roundtop valley | - | 0 | 0 | 0 | 0 | 0 |
| Mt. Tremblant ridge | 0 | 0 | 1.0 | 0.3 | 0 | 0.3 |
| Montmorency summit | - | 0 | 0.9 | 0 | 0 | 0.3 |

Table 3. Percentage of observation hours with ozone concentrations > 80 ppb.

| | May | June | July | August | September | Season |
|---|---|---|---|---|---|---|
| Roundtop ridge mean | 44.5 | 40.9 | 39.0 | 42.3 | 34.2 | 40.0 |
| max. | 86.9 | 93.4 | 90.8 | 73.2 | 77.0 | 93.4 |
| Roundtop valley mean | - | 21.0 | 22.6 | 24.5 | 19.4 | 22.6 |
| max. | - | 36.8 | 69.4 | 70.0 | 68.7 | 70.0 |
| Mt. Tremblant ridge mean | 40.7 | 37.0 | 34.2 | 34.5 | 23.8 | 33.7 |
| max. | 79.3 | 86.8 | 89.5 | 85.1 | 71.6 | 89.5 |
| Montmorency summit mean | - | 33.5 | 29.0 | 32.0 | 24.5 | 29.5 |
| max. | - | 79.0 | 95.4 | 66.3 | 59.5 | 95.4 |

Table 4. Mean and maximum ozone concentrations (in ppb) by month and season for each site.

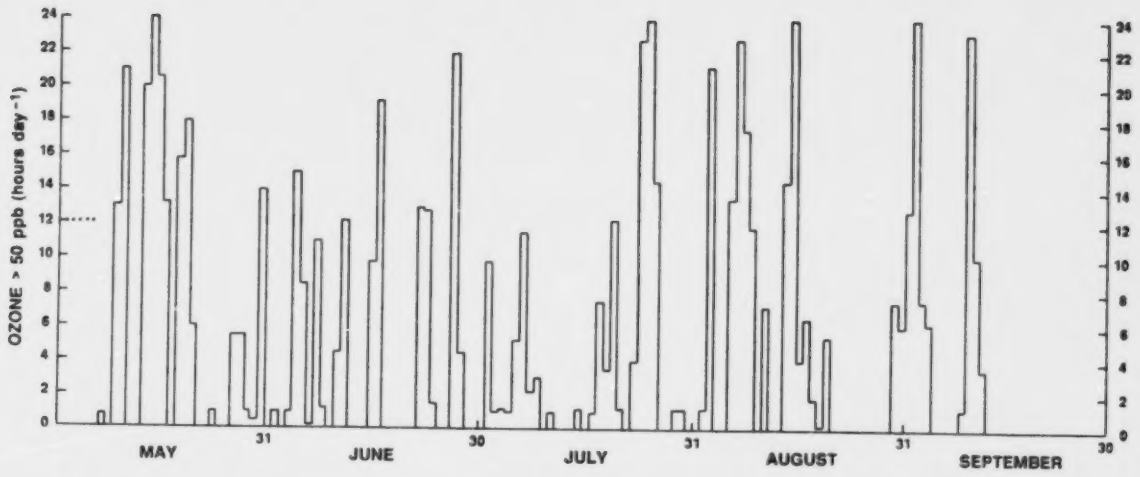


Figure 1. Number of hours per day with ozone concentrations > 50 ppb at the Roundtop ridge location (845m). The dots (...) indicate data are missing.

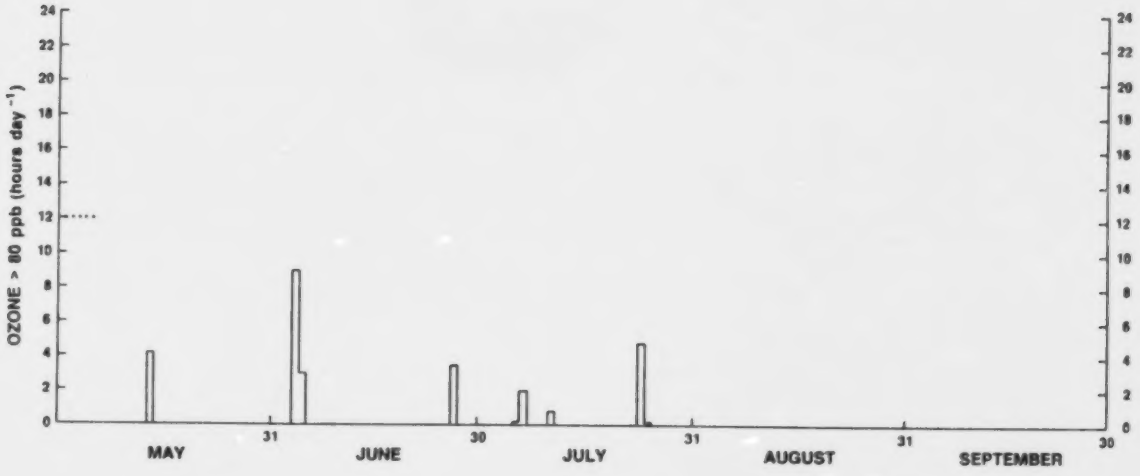


Figure 2. Number of hours per day with ozone concentrations > 80 ppb at the Roudtop ridge location (845m). The dots (...) indicate data are missing.

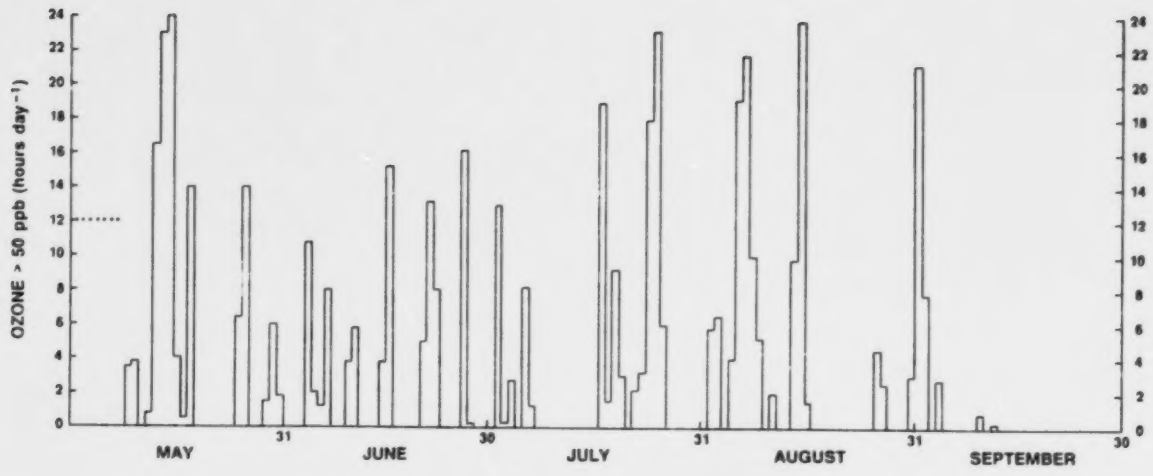


Figure 3. Number of hours per day with ozone concentrations >50 ppb at the Mt. Tremblant ridge location (860m). The dots indicate data are missing.

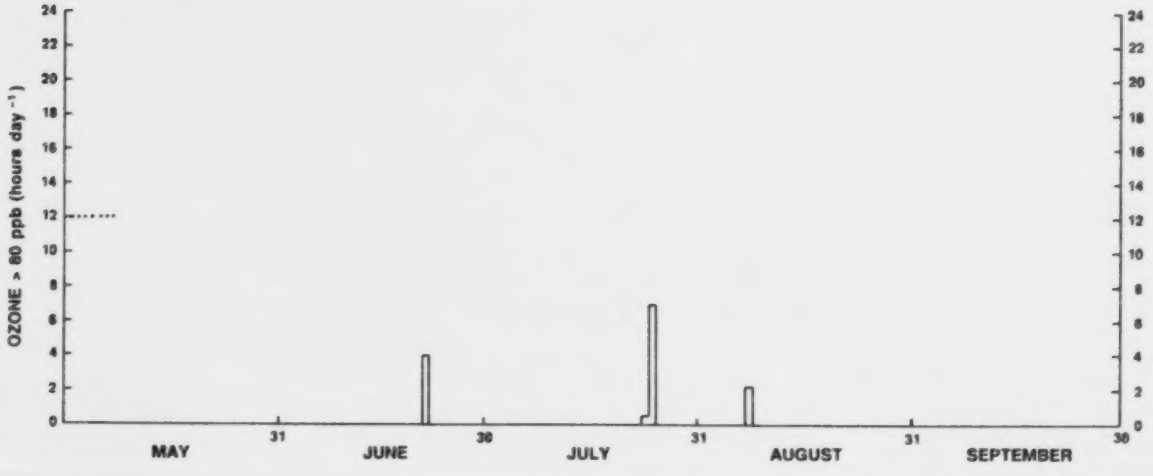


Figure 4. Number of hours per day with ozone concentrations >80 ppb at the Mt. Tremblant ridge location (860m). The dots (...) indicate data are missing.

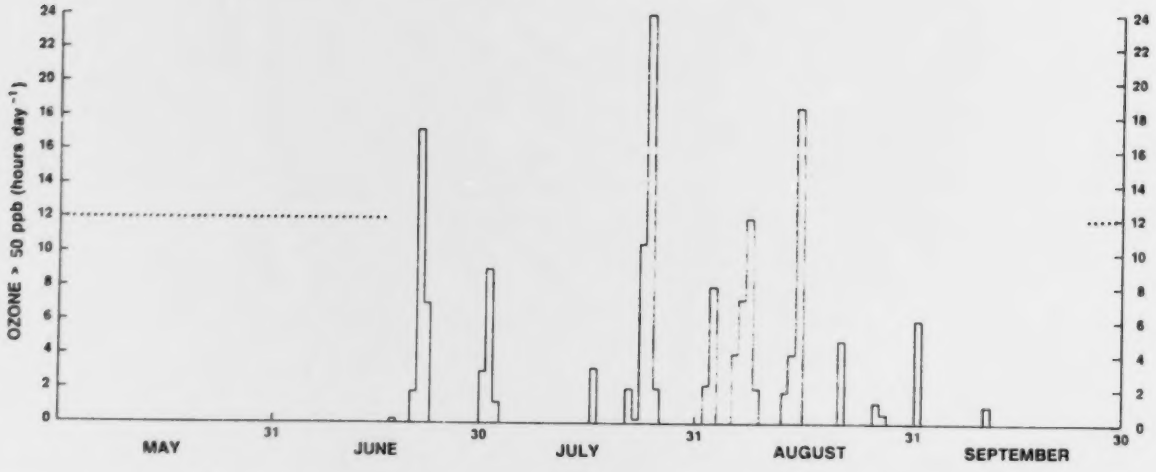


Figure 5. Number of hours per day with ozone concentrations > 50 ppb at the Montmorency summit location (970m). The dots (...) indicate data are missing.

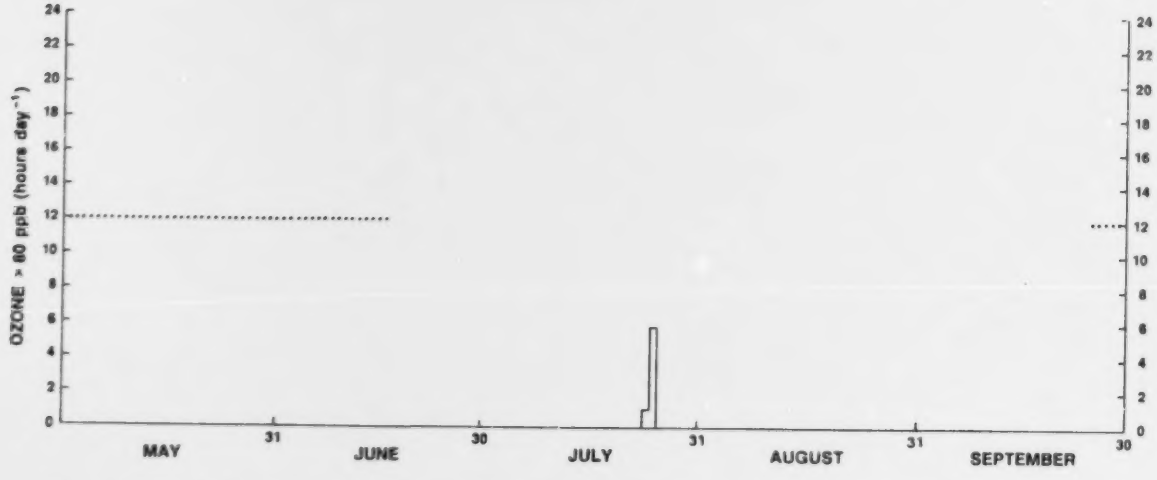


Figure 6. Number of hours per day with ozone concentratios > 80 ppb at the Montmorency summit location (970m). The dots (...) indicate data are missing.

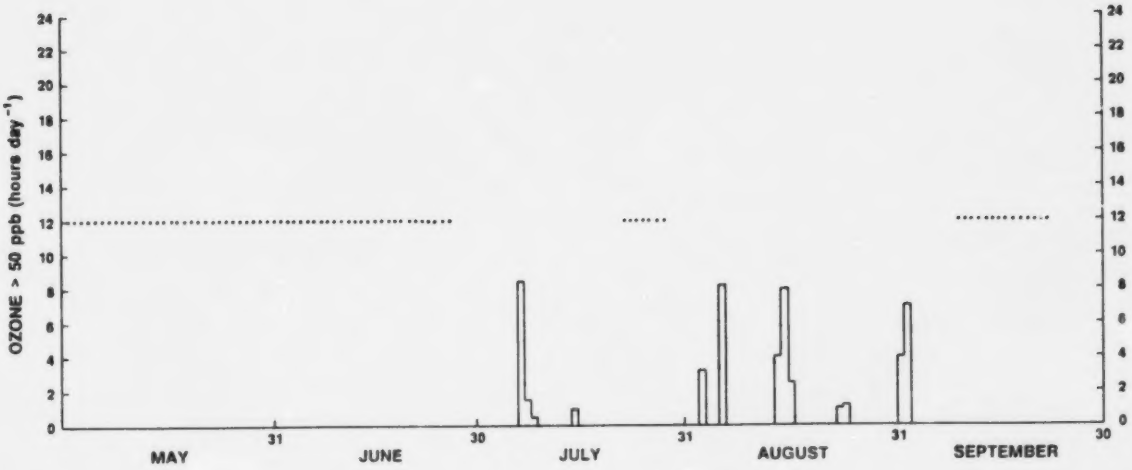


Figure 7. Number of hours per day with ozone concentrations >50 ppb at the Roundtop valley location (250m). The dots (...) indicate data are missing.

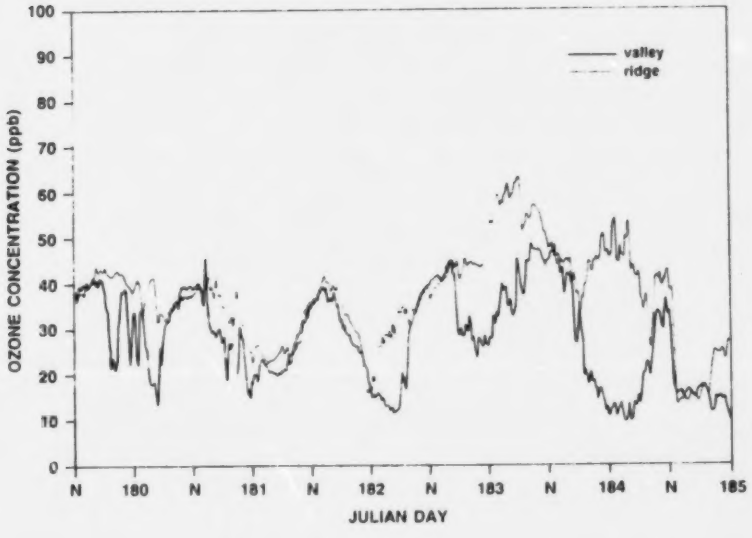


Figure 8. Ozone concentrations for a 5.5 day period starting at noon (N) on 28 June 1986 and ending at midnight on 3 July (0000, day 185). Data are for the Roundtop Mtn. ridge (845m) and valley (250m) locations.

# ALLOCUTION PRONONCÉE PAR LE MINISTRE DE L'ENVIRONNEMENT DU QUÉBEC

M. Clifford Lincoln

Monsieur le Président de cette illustre rencontre
Distinguished guests from the United States and all parts of Canada

Je vous souhaite la plus cordiale des bienvenues à Québec, la ville même qui est l'âme et le coeur du Canada - ville historique entre toutes. Je vous souhaite une bienvenue d'autant plus cordiale que par vos connaissances, vous nous apportez une contribution particulièrement précieuse, car elle débouche sur l'amélioration de notre qualité de vie, la nôtre et celle de ceux qui vont nous suivre.

Je pense ce soir à une personne qui s'appelait Thérèse Gagné; c'est un nom qui est très familier à tous - il y a beaucoup de Thérèse et de Gagné au Québec. Elle habitait la Beauce, une région tout près de Québec, comme vous le savez. Et là, elle avait vécu dans un lieu pour elle, idilique, entouré d'érablières, de magnifiques forêts d'érables. Cette petite Thérèse Gagné avait un talent naturel, celui de pouvoir peindre la glorieuse nature qui l'entourait. Elle aimait tant peindre ces magnifiques arbres, ces érables, qu'elle en arriva à devenir un peintre très connu dans la région. Elle donnait ses peintures, elle les vendait aussi, jusqu'au jour où mariée, à l'âge d'environ 30 ans, son mari, ingénieur, était transféré aux États-Unis, en Californie, où il s'établit, très loin de la terre natale. Thérèse Gagné aimait la Californie mais rêvait toujours à la Beauce, aux érablières, à la ferme où elle avait vécu, où elle avait peint tant de magnifiques tableaux de cette magnifique nature beauceronne. Son mari mourut en 1984, et là, devenue une vieille femme, un demi-siècle après avoir quitté sa Beauce natale, elle y revint, ayant le désir de retrouver et de peindre à nouveau sur ses vieux jours, ce qu'elle avait connu et tant aimé. Mais là, ce fut la consternation. Les arbres qu'elle avait connus sur la ferme de son père n'y étaient plus; les arbres, s'ils n'avaient pas disparu, étaient tellement malades qu'ils auraient pu n'être plus là pour autant. Et cette consternation, c'est la même que vivent les gens de cette même Beauce, où les érablières - l'érable, le symbole même du Québec et du Canada - n'existent plus ou dépérissent de jour en jour devant leurs yeux.

This lady, Thérèse Gagné, I invented her. She never existed, and I imagined her story, because it could easily have been a true story. I was recently reading a book about atmospheric pollution by Ross Howard and Michael Perley. And in the preface to the book, the authors described how one of our great Canadian painters, A.Y. Jackson of the famous Groupe of Seven - used to go and paint in Northern Ontario, by the shores of a beautiful lake, called Lake Nellie, in Killarney Park. And there, he painted one of the most famous scenes in all of Canada, a scene that eventually people would see everywhere on calendars, and on stamps, a painting beautifully descriptive of the Northern Canadian landscape, with its magnificent trees and lake, where fish abounded. And Ross Howard and Michael Perley tell us that if A.Y. Jackson had come back 20 years ago, in the 1960's, the setting would have been very different because the lake now is dead. There are no fish in the lake anymore. The trees are sick and the water is translucent, because the water is dead. This is a story that anyone of us here today, whether we be Americans from California or Minnesota or Vermont, or Canadians from Quebec or Ontario, could tell in our own way. Each one of us could tell his or her own little story about how, his or her own lake, his or her own forest, is affected today.

Je voudrais profiter de l'occasion pour vous saluer tous ici, très respectueusement et avec beaucoup de fierté. Oui, nous qui vivons ici au Québec, qui vivons tous les jours dans cette belle et magnifique ville de Québec qui est la capitale de notre province, qui est le berceau historique du Canada et qui en sommes très, très fiers, nous sommes particulièrement heureux de vous voir ici, vous, un groupe de personnes éminentes par vos connaissances scientifiques. Nous nous réjouissons que vous soyez venus, vous qui vous êtes déplacés de si loin, some from California and some from France, vous qui êtes venus de tellement loin pour nous rencontrer ici et nous aider à parfaire nos connaissances de ces substances toxiques qui affectent notre qualité de vie de tellement près tous les jours. Nous sommes fiers que vous ayez choisi Québec, le Québec et le Canada pour cette première conférence sur les oxydants.

So we welcome you, very, very especially for having chosen Quebec for the first symposium on oxidants in North America. This follows the very successful conference we had in Quebec on acid rain some two years ago. Somehow we feel and we hope that Quebec, why not Quebec City, will become the capital of the environment, where people from all different walks of scientific life and ecological life and day-to-day life will come and gather to discuss problems relating to our quality of life and that of the generations to come. Quebec City is especially dear to us. Last year, it became the first North American city to be chosen by the United Nations as a world-heritage city. The first North American city of this kind. Within its historical walls, that are hallowed walls to Canadians and Quebecers, there lie several centuries of history, the history of people of different languages and creeds that have learned to live together in harmony. And maybe these walls are symbolic as well, because today walls like these and the beautiful statues, magnificent historic relics that grace this city, are also damaged by the atmospheric polluants carried from state to state and from province to province. So maybe Quebec City is symbolic of many things. A very old city, lying proudly on its cliffs, that says to us: "I want to preserve what I've got of the past and at the same time, I want to build for the future, because I want to continue to live in the 20th Century and to share in the 21st Century". This, I think, is the big challenge that this city presents to us through its blend of historical magnificence and modern technology. If we look around us, man - 20th Century man - and I say man in the broad sense (I certainly don't want to offend women, women who carried us all forward because they suffered so much over the generations, while men could invent and build, while enjoying the greatest freedom of action.) Thank goodness, the world has changed...Yes, 20th Century man has been exceptionally inventive and creative, a builder of genius.

L'homme de notre siècle a fait des choses tellement remarquables qu'on ne peut plus les nommer: le laser, l'ordinateur omniprésent, la fibre optique, que sais-je! Aujourd'hui, ce monsieur est sorti de la France, est venu ici, en jet. Il a pris à peine quelques heures pour un voyage qui, dans les années 50, aurait pris 6 ou 7 jours en bâteau et du temps de mon père, peut-être un mois. Aujourd'hui, on voyage dans l'espace, on expédie des satellites qui vont photographier Vénus et Mars et nous renvoient des images si vivantes qu'on se croirait tout près de ces astres. Aujourd'hui, nous regardons la télévision transmise par satellite et nous pouvons suivre la course de bâteaux de la Coupe America en Australie. Nous avons réussi des exploits remarquables tant dans le domaine scientifique que dans le domaine médical, culturel ou social. L'homme a été une créature d'invention et de génie, surtout dans cette deuxième partie du 20ième siècle, qui a malheureusement connu de terribles guerres, lesquelles ont cependant provoqué une effervescence scientifique.

It is this same man, this genius of creation and invention, who can now send people into space, who can set up space-stations where individuals can live for days and even months. Indeed, space-exploration seemed almost part of man's day-to-day life until American astronauts so sadly went into the sea off Florida. Till then, we used to take space-launches so much for granted that we never used to look at them on T.V. anymore. It was part of the regular scene: space-ships simply went up and came down, and we used to think that nothing would ever happen to them because man created such perfect instruments of technological life.

And yet, that same man who has created so many marvels of technology has also been man the destroyer of his own ecology, of his own natural heritage. We only have to look around us and see what has happened over the generations, especially during this century, a century at the beginning of which man took over a planet that was covered almost for its two thirds by a green cover and now

lives on a planet where barely half of that green cover is left - where our natural forests and our tropical forests are being cut back or are dying so fast that certain experts hold that in some parts of the world the process is about to become irreversible. We peer across the oceans and we see what is happening in Africa where people are dying of hunger because we have created more and more deserts. Even closer to home, we are creating deserts without even noticing it, because it's happening gradually. Soon, when we will wake up and take notice, it may be too late. Yes, it is this same man of genius who is creating wonderful technological life, whilst killing precious natural life. As an example, take the Beluga whales in the St. Lawrence River, these marvels of nature: there used to be 5 000 some years ago, now there are barely five hundred. Now it can be said they are not only endangered species but also dangerous species, because if they drifted on to the shore, they could spread the toxics they're carrying - mirex and so many others. So I wonder sadly, and often ask people that I address from time to time: What would it be like if a young boy that might have lived in 1887 and not 1987, and was 12 years old then, if that young boy came back to our world and went back home to Ohio or California or Minnesota or Vermont, or Quebec or Ontario, or British Columbia or any other place on the North American continent. He would come back and say: I want to visit where I used to live and see what it's now like. He used to really enjoy his surroundings throughly, and if he came back, say to the shores of Lake St. Louis next to Montreal, he would look for the forest where he found shade in the middle of the day during the summer, and the forest would be gone. Instead, there would be brickwalls and big mansions right there on the shores, where the land is eroding fast. And the boy would want to fish and would be told: "Don't fish there because if you catch any fish, you will not be able to eat it; it's all contaminated." He might say: "Well, I would just love to swim where I used to swim" and he would be told: "Don't swim there, if you get scratched, the wound will fester." If he went on to drink the water, he would be told: "Hey, don't do that, it's the last thing you should do.

That water is totally polluted". All of this is certainly true of Lake St. Louis and I'm sure it reflects the picture not just here but all over the place. And this young boy should ask us all: "Is this the kind of land that I left you? Is this the kind of heritage that I left you? Why have you spoiled it all so badly? Why have you been so negligent and so lax with the heritage I left you that today the trees are gone, the water is polluted and fish-life and bird-life are disappearing?" And I wonder who is to blame? Certainly not the generation of the 1887 boy ! So we, of the present generation, built a wonderful world of technology and profits and efficient factories; but what happens to the quality of life that has to wind its precarious way around all those buildings and walls and technological marvels?

J'étais en Suisse récemment pour une visite avec certains de mes collègues du ministère, qui sont présents ici aujourd'hui. Nous sommes allés visiter une forêt affectée par les polluants atmosphériques, à côté de Berne, guidés par un des éminents forestiers suisses, M. Louis de Coulon. Et ce même jour, par une étrange coïncidence, M. de Coulon allait nous quitter pour participer à une conférence de presse où il allait annoncer que 50% de la forêt suisse - la ressource la plus précieuse pour la Suisse, car elle touche les fibres mêmes du peuple Suisse - que 50% de la forêt suisse, dis-je, était endommagée par les polluants atmosphériques. Oui, 50% de la forêt suisse! Et je me souviens d'un rapport que nous avait remis M. de Coulon et ses collègues, un rapport qui affichait des statistiques presque effarants. Dans ce rapport suisse, il est démontré que les Allemands de l'Ouest, dans une étude qui va être rendue officielle bientôt, estiment que les dommages causés aux forêts allemandes par les polluants atmosphériques sont si graves qu'il coûte à l'Allemagne en perte de revenus touristiques, déficits forestiers, érosion du sol, etc., 18 milliards de marks allemands par an - yes, 18 billion Deutch marks a year due to forest dieback. And this German study will show - and I was going over the figures tonight to make

sure that I didn't get them wrong, that if the same trends continue unabated, then, the cost to the German economy, for the forests alone, by the year 2060, would be 341 billion Deutsch marks. Even if the pollution were reduced by a significant degree - they, dit not indicate by how much - then, the cost would be 249 billion Deutsch marks! The same Swiss report, published in 1985, also indicated that ozone damage to Swiss crops (fruits and vegetables) ranged between 565 million Swiss francs and 990 million Swiss francs a year. Yes, a high figure of nearly a billion Swiss francs a year! In a U.S. study quoted in the Swiss report - and that finding because it applies to human beings is even more dramatic than statistics on forests and apples and vegetables - it was shown that if the U.S. could have reduced its atmospheric pollution by 70% (this was a 1979 study taking 1970 standards as the starting point) - if it could have reduced by 70% then, the U.S. could have saved itself, right off, 40 billion U.S. dollars. So the economic figures up and down are huge but unfortunately far more than figures and statistics are involved.

Les humains ne sont pas des chiffres et rien n'est plus précieux que la vie humaine. Pourtant, j'ai visité des endroits, j'ai visité des endroits ici même au Québec, une ville ici même au Québec où les travailleurs dans l'usine portent des masques d'oxygène. J'en ai porté moi-même ainsi que mon collègue ici, lui aussi. On ne peut pas entrer dans certaines parties de l'usine sans masque à oxygène. Là, j'ai causé avec des gens qui m'ont dit: "Monsieur, quand je circule dans la ville, je tousse et je ne me sens pas bien. Avez-vous le droit, vous, comme gouvernement, de nous obliger à endurer cela pendant encore bien longtemps?" Et cela vous donne à réfléchir, cela vous fait réfléchir et vous vous demandez si nous n'avons pas perdu le nord? Vous vous demandez si nous avons construit une société si égoïste que nous ne pensons que peu souvent à ces choses - pas

seulement aux forêts, pas seulement aux arbres, pas seulement aux lacs, pas seulement aux poissons, pas seulement aux oiseaux, pas seulement aux marsouins, pas seulement aux baleines, mais aussi et surtout à la personne humaine qui souffre de plus en plus à cause de notre incurie. Il faut que nous nous mettions à y réfléchir, surtout que nous les humains avons le choix et le pouvoir de décider du monde que nous allons façonner pour nous-mêmes.

I wonder sometimes about the relation between greed and need. Indeed, when I read about places such as parts of Africa where starvation affects hundreds of thousands of people or maybe more, when I see T.V. documentaries depicting desolate lands without any trees in sight and little water anywhere... When I read reports from the United Nations and other agencies that some states in Western Africa have depleted their natural tropical forests by 50% or more in the last fifteen or twenty years...When I reflect on all this, I reflect that on one hand the motivation is greed to sell their natural resources recklessly, and on the other hand, the motivation is need by people who are left with no alternative but to use the few resources that have been left to them. They are forced to use the last little supply of water, because there is no other water left for them. They are forced to cut the very last tree there is, because no trees have been left for them by those who had the choice between leaving trees or cutting trees. So the question we must ask ourselves is this: "What is our responsibility, we that have the choice to make; we who hold the power to make that choice in regard to the person who doesn't have that choice and must suffer from the consequences of our decision?" - This, I think, is the challenging question facing us to-day.

I remember years back - I was born outside of Canada in a little British colony - I remember as a very small boy how one of my uncles had kept in his garage, a model of one of his first cars. I don't know how far back that model sprang, but it was a very old car even then. I remember

it to this day, and that's many years ago, when I was still small. It was a formidable looking contraption, an antique which today would be worth a lot of money. Cars were rustic and a real luxury when I was small. Yet, today, cars are everywhere. I went to one of the Carribean Islands recently and cars were here, there and everywhere - small, smaller and smaller still, thousands of them. In the United States, there are millions and millions of cars everywhere. Cars are a way of life. In my own driveway, my daughter has got a car, we have got two cars, that makes three cars. In some families, there may be four cars, and we take it for granted: two cars, three cars, or four cars - it's part of everyday-life.

I remember once when one of my own brothers took a flight to another country. Flying was a big event then. I remember my mother cried. My brother was going away to study somewhere, and he took a Super Constellation. It was quite a plane then and I used to stare at it and marvel about this huge new plane. Today, I am sure, none of us would take a Super Constellation to go anywhere! My uncle's strange car was a Super Constellation of its day. Now, jets criss-cross the skies in all directions and there are so many thousands of planes landing in Chicago and elsewhere that planes have tosometimes stack up for miles awaiting a chance to land.

Et là, nous avons tellement expédié d'engins dans l'espace que les avions sont devenus les autos de l'air. Demain, allons-nous envoyer dans l'espace autant d'engins que les automobiles d'aujourd'hui? Allons-nous créer dans l'espace les mêmes problèmes que nous avons créé ici avec l'auto? Nous avons déjà découvert que nous avions perforé la tranche de protection d'ozone qui filtre les rayons du soleil et malgré cela, nous continuons à expédier tous les jours des avions, des engins, dans le ciel, sans jamais penser aux conséquences , comme nous faisions jadis ici avec les autos. Et les autos, qu'est-ce qui nous est arrivé avec les autos? Je me souviens d'un ami à moi, Bruce Walker dont

j'ai vu le nom sur la liste d'invitês de ce soir. I don't know if Bruce is here tonight. He used to tell me years ago, when I was Opposition critic for the environment: "Cliff, you have got to do something about cars, if you ever win the elections." It has happened; we won the elections. When Bruce used to press me about the car emission problem, I used to think: "Well, Bruce, he's a nice guy, but he's got carried away." I wasn't concious of the magnitude of the problem then. On that recent trip to Switzerland, I came across Swiss statistics which indicate that N.O. X. car emissions in Switzerland in 1950 were (I'll look up the figures again so that I don't mislead you, I have written them on a little piece of paper so as not to mislead you. I'll find my piece of paper and I'll find my glasses because I have got to this age where I can't read anymore without them...Here goes.) So...O.K. In 1950, 9,600 tons. In 1960, 30,600 tons.In 1984, 157,000 tons!! Using my little mathematical knowledge from my schooldays, I workd it out to be a 1643% increase in 34 years. Whow! If we ever do the equivalent upstairs, with the planes, God help us! So this is what we have done to ourselves. Nobody else has done it. The paradox of us smart guys - I say guys because I won't include the ladies - the ladies are far too sensitive and kind and gentle and clever to have done what we did. Yes, we, the smart guys, we did it. Oh yeah, we're smart, we are going to build, we are going to press on regardless, we're going to put that wall there regardless. Then, we will realize afterwards that maybe it was all a little too fast, a little too soon, without thought as to the consequences. So the paradox of us men, is this, that up there where we need an ozone layer, we're puncturing it. Down here, where we don't need ozone, we're building it. I'm not a scientific person, but like you, I am a very deeply committed and convinced person about the quality of life that I want to leave to my children and their children.

Little things strike you sometimes. My Press Attachē, Mary-Andrēe Jobin, who is here to-night and who is conscious of the ecology and very committed to try and change attitudes in the younger generation, was telling me about a song with an ecological message by a famous French singer, Yves Montand. The lyrics are so beautiful that I'm going to read excerpts to you. I'm terribly sorry that some of you don't understand French, but it might sound nice all the same, even with my wrong accent. This is about a little girl and an old man that are walking along the banks of the Seine in Paris - those of you who know Paris, know how beautiful the Seine is. And the song goes like this:

"Qu'il fait beau
l'eau sale a des reflets gluants d'apollinaire
de verlaine, de pernod, (etc.)

"Quai d'Issy
Des bouffées de pētrole
Achēvent un vieux saule
Et cinq ou six troēnes (etc.)

En ēcho
De clamart à Vincennes
Et sur le front de Seine
Le bēton a surgi

Et l'enfant
Soudain me dit: Monsieur,
Mais qu'avait-il de mieux
Ton Paris d'autrefois?

The old man replies:
"Mais qu'avait-il de mieux?
Mon enfant, je n'sais pas
Peut-ētre ici oū là
Simplement, du lilas...

And the little girl answers:
"Du lilas? Du lilas?
Qu'est-ce que c'est du lilas?"

Qu'est-ce que c'est que du lilas? Indeed, how can lilacs exist for somebody that has never seen them? I know what it's like when we go through a grieving period, when we visit a place we all hate to visit, a funeral home, on the occasion of a dear friend's death. It's a terrible feeling. We would like the sad event to simply go away. The grief is immense, and all the more immense and real the closer the person is to us. It is that deep, our grief, because the moment is so final - the person was with us yesterday and is not there today. And yet, even if I grieve for the state of our ecology today, if I grieve for the destruction wreaked on ourselves, I still have great optimism in the future. My grief is not of the same type as that which affects me when a dear one passes away because I know that in this case, it is a passing phase and that we are determined to make it a passing phase. This is why you are here today and why I am here today. In other words, I view the state of what we have imposed upon ourselves like a deep winter.

L'automne est venu, les feuilles sont tombées, mais nous n'avons jamais cru que l'hiver suivrait. Puis l'hiver est venu et l'hiver est resté et l'hiver a continué... la noirceur totale, plus de feuilles sur les arbres et nous nous sommes dits: "Mais cet hiver-là, ça va durer combien de temps?"

Indeed! It has been a deep winter after a long fall. The fall was there and the signs were there and we never paid heed even as the leaves would fall from the trees in so many areas all across our lands. We never looked, and we said: "Oh, winter can't happen here...(in Quebec we should know better!) But winter happened and winter is still here. It's going to be a long, long winter. Yes, it is up to us to bring about a revival, contrary to the case of our dear friends. This time, it is up to us to turn things around and make spring happen again - the ecological spring. I believe in the ecological spring. I believe in it deeply

because of you who have got the power of collecting knowledge, of tracing the causes and the roots of problems and making us aware of them, so that we, in turn, can join this great crusade. Thus can all of us together turn things around and make the ecological spring happen. It's not going to happen overnight, but it's going to happen if all of us believe in it together.

Just one more little story, if I may. I belong to the Liberal Party of Quebec and the President of the Liberal Party is a fellow called Robert Benoît, a bright young executive: I mean young by my standards. He must be 35 or something like this, and he has a little daughter of 8 years of age called Valérie. He was pointing out to me the other day how mentalities have changed and are changing from his young days to her young days. Valérie was driving along with her father, and Robert said to her: "Valérie, what do you want to be when you grow up?" And she said: "I want to be the President of the Liberal Party of Quebec." And he said: "Well, that's nice. What are you going to do as President of the Liberal Party of Quebec?" She said: "Oh, I would just love that... I would clean up our lakes, I would plant trees, I would clean up nature all around us. I would send messages around the world, asking people to clean up the lakes and plant trees and make nature grow again."

And I hear the same message more and more, as I visit schools and see that the eight year-old children of today are not the way I was when I was eight- not the way my own children were when they were eight because I never knew how to inform them any better. Today - les nouvelles générations se réveillent à cause de vous qui passez le message qu'il faut se réveiller. Le message que le monde d'aujourd'hui n'a plus de frontières géographiques, de frontières artificielles, de frontières séparant le reste du Québec de l'Ontario, du Vermont. Nous sommes tous assujettis à la même pollution qui dépasse les frontières, qui dépasse les continents. En fait, je lisais un article du Professeur Louis Rey qui indiquait que la pollution atmosphérique voyageait de la Russie à nos territoires de l'Arctique. D'où la pollution vient, nous ne le savons jamais.

Today, we face a planet problem. It's no longer a U.S. problem, a Canadian problem, or a French problem, or a Swiss problem, or a German problem, or an Indian problem. These days, I hope, are gone. We must realize that we have got to look at the world as one planet where pollution is not confined to us as if for us in Quebec it's our pollution and if you're in Ontario, it's your pollution. It's our pollution all of us, and it's our common pollution and we've got to accept that it is. And with all due respect, and I say it with the greatest kidness and respect because I realize that my place is to be Environmental Minister of Quebec and not to say anything that will offend; I don't mean it that way at all, and I want to be quite clear on that. At the same time, I feel I've got a duty to say what our citizens feel very, very deeply here, that we sense in Canada, that on the question of atmospheric pollution that travels from border to border - there is a clear lack of response from our great friends down south. We don't get that sense of response to our concerns that a real problem exists today, not tomorrow. That the solution is not the fruit of what we can do in ten years time. We say the problem needs solving today, that the lady who painted trees and whom I described earlier, would find there is a grave problem now. I know because I've seen it for myself. He who would seek to find out, would find out that what I've said about the workers in the plant is true. I know because I've seen it for myself. What we feel and say here, is that we're trying to clean up our own glass house before throwing stones. What we say here is that we're trying our hardest to cure the problem as much as we can, that the provinces of Canada and the Federal Government have joined in on an Acid Rain Agreement where we have set targets for ourselves. We have committed ourselves by 1994 to reduce our emissions by 50%. Maybe 50% is not enough, and I agree - I hope it will reach 90% within a reasonable future. At the same time, 50% is a standard, and a goal and indeed, a high standard. It is a difficult and realistic target and I hope we reach it as I know we will. In Quebec, we have gone beyond our word, because I can commit myself to say that a

good four years ahead of the Canadian schedule, we will have reached our target. In fact, in a matter of some days, maybe two weeks, maybe three weeks, we're going to sign a very, very important agreement - important in fact as well as symbolically. It involves our largest acid-rain polluter within Quebec, representing 50% of the atmospheric pollution we produce ourselves. The Quebec Government and the Federal Government acting in unison, will sign an agreement to extend loans to this particular industry which will agree to reduce its emissions by 50% by the beginning of 1990 - January 1990. thus by early 1990 in Quebec, we'll have reached our Canadian target, as I say four years ahead of the Canadian schedule, which is 1994. I hope that if I'm still in this job in 1994 - Goodness knows? - ...politics!!! it's a strange world... Anyway, I hope that in my absence the person who replaces me will have reached 60% or 70% by 1994. May I say in the most friendly way to our American friends who are in a great majority here, and say it kindly and with all humility: I cannot agree with the contention that no targets should be set. You should take the leadership in this rather than us Canadians who are nowhere as powerful and strong as you. When you took the leadership - for instance in the case of car emissions - and this is why may I cited the example of Switzerland...when you took that leadership, you didn't wait while you found out exactly how it could be done and whether it could work first. You told the auto manufacturers: "Listen, by a certain day and time, you must do something about emissions and reduce them substantially, and it is up to you to find out how to do it"... And the car manufacturers did. I know there is a representative of General Motors here - it's not criticism that I utter, on the contrary, I salute the automobile-industry because it made wonderful strides forward when it reduced car emissions drastically and cured its ills. The U.S. became the leaders not only in North America but around the world, when the French, the Swiss and the Germans (they who make and sell the prestigious Mercedes and all the other beautiful cars that cost eighty thousand or ninety thousand dollars) were left far behind where it counted and whilst you in America had solved the critical problem years and years ahead.

America should be the natural acid-rain leader and it should be telling us: We have the power, the knowledge, the university system, the wealth, the size, so that we can do it far ahead of you. We have the clout to tell our industry to do it, and they shall do it. Yes, I believe very strongly that you could be that great leader worldwide and that if you wanted to, you could beat us to it and reach 90% and more by 1994. This I certainly urge you to do.

I have kept you long enough but I want to say in closing that I believe very, very deeply that what we must look for, is not only a free-trade agreement between the United States and Canada. Commerce is not enough - we must make sure that we strive for ecological free-trade between us. Were we to arive at a successful free-trade agreement, yet lose our trees and our lakes, somehow it would have been in vain.

The type of ecological free-trade agreement we must seek must include avoiding to send to others what we don't want to tolerate for ourselves at home. So, I urge each one of you, wherever you be from - the United States or Canada or France, to - each return back home, resolved, through having met together here, that there is a common cause that is much bigger than us all; to return home and resolve that each one of us has got a job to do, to sell the idea of the ecological spring to our neighbor so that eventually, from the minorty that we were years ago, we will turn into the big majority that increasingly we are becoming.

Le monde est en train de changer. Les humains ne tolèreront plus une qualitè de vie inférieure à ce qu'ils auraient pu avoir connu s'ils avcaient vêcu ici il y a bien des années de cela. Les jeunes ne veulent plus tolérer que nous leur laissions un hêritage naturel amoindri, dêtruit et saccagé.

Les jeunes s'attendent ã ce que nous fassions tout ce qu'il faut faire pour leur laisser une qualitẽ de vie saine, profitable et durable; un hẽritage de ressources naturelles dont ils seront fiers et dont ils pourront jouir.

The young generation expects many, many things of us. They certainly expect of us to get rid of the deep ecological winter and make the ecological spring happen, and happen very fast. And I urge you all together, we and you, to make it happen.

Thank you.

CINQUIÈME SÉANCE/SESSION V

CONCLUSIONS ET RECOMMANDATIONS/CONCLUSIONS AND RECOMMENDATIONS

Président/Chairman

Jean Piette
Direction des relations intergouvernementales
Ministère de l'Environnement du Québec

# EFFETS SUR LA SANTÉ HUMAINE ET LES ÉCOSYSTÈMES TERRESTRES/SUMMARY OF OXIDANT RELATED HEALTH AND TERRESTRIAL EFFECTS

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Summary of Oxidant Related Health and Terrestrial Effects
Presented by Michael J. Bradley
at the
North American Oxidant Symposium
February 27, 1987

Good morning! I intend to summarize the documented effects of ozone on human health and terrestrial ecosystems and to reflect on the questions these effects raise for scientists and environmental policy decision makers. To begin, I would like to share with you my firsthand encounters with the effects of air pollution during the early stages of my career in air quality management. In 1979 I traveled to Juneau, Alaska to begin my first air quality control position with the Alaska Department of Environmental Conservation. Soon after I settled into my new job I was sent to Los Angeles to attend a training course. While in Los Angeles I decided to take advantage of the warm weather to go jogging. I had not run very far when I was overcome by coughing and shortness of breath. I learned later that an air pollution alert was in affect in Los Angeles and that the ozone levels were almost three times the National Ambient Air Quality Standard. After four days, I was happy to escape Los Angeles and return to the clean, moist air of southeast Alaska.

Much of southeast Alaska could almost be considered a rain forest because of the almost continuous rainfall and lush growth. Dense forests of tall cedar, spruce, and hemlock cover the steep slopes rising out of the thousands of channels and bays which make up the Alexander Archipelago. These forests supply trees to several pulp and lumber mills in southeast Alaska.

I will never forget my first visit to the pulp mill in Ketchikan. We drove along the shore of a protected cove and as we rounded a sharp curve, I was struck by a strange sight- most of trees on the hillside ahead were dead. The slopes were covered with the skeletons of thousands and thousands of dead trees. When I questioned them, the officials at the pulp mill insisted that the trees were dead <u>before</u> the

construction of the pulp mill. Because I had not seen any other area in southeast Alaska with any signs of forest dieback, I found it difficult to accept this explanation.

Several weeks later I was assisting with the inspection of another pulp mill located in Sitka, Alaska. To my surprise, I found the forest surrounding the pulp mill in exactly the same devastated condition as I had seen in Ketchikan. The officials at the Sitka pulp mill explained that they were studying the situation to determine if emissions from the pulp mill played a role in damaging the trees. They stated that as of that date they had found no connection between the pulp mill and the condition of the surrounding forest. To me, the association was quite clear.

On the first day of this symposium, Dr. David Bates, Dr. Bernard Bernier and Dr. John Skelly eloquently described the public health and terrestrial effects of exposure to ozone. In their presentations, they raised the serious question of whether the current United States National Ambient Air Quality Standard of 0.12 parts per million is adequate to protect both human health and terrestrial ecosystems. Scientific evidence clearly indicates that exposure to ozone concentrations at or just above the current United States Ambient ozone standard adversely affects public health. According to the U.S. Environmental Protection Agency, healthy individuals who are exercising while ambient ozone levels are at or slightly above the 0.12 ppm U.S. Standard can experience reduced lung functioning leading to "chest pain, coughing, wheezing, pulmonary and nasal congestion, labored breathing, sore throat, nausea, and faster respiratory rate". The U.S. EPA also found that children exposed to ozone conditions similar to those which occur during ozone episodes in the northeastern U.S. experience decrements to lung function which can persist for many days after the ozone episode has passed. Moreover, animal toxicity studies reveal that elevated ozone exposures can inflict damage to sensitive lung tissue and that long periods of exposure to elevated ozone can cause permanent lung damage. Animal studies have illustrated that even ozone exposures at concentrations well below (0.12 ppm) the current U.S. standard can

result in increased susceptibility to acute respiratory infection.

In my mind these studies justify a more restrictive ambient ozone standard, such as the one hour .08 ppm standard established by the Province of Quebec and the State of Maine. At a minimun, an appropriate eight-hour ozone standard should be established. This would more accurately reflect the common duration of public exposure during the annual ozone season in the northeastern United States.

Dr. John Skelly presented an excellent overview of the current scientific understanding of potential forest damage caused by exposure to ozone. Clearly there is a growing body of scientific literature which implicates ozone as a contributor to widespread forest damage and to the documented growth decline in a few specific species. As Dr. Skelly indicated, forest damage from ozone is dependent on two major factors: the level of ozone exposure and the duration of ozone exposure. Some of the damage ozone can inflict on forest ecosystems is visible such as discoloration of foliage. Other damage is less obvious but equally serious, including reductions in photosynthesis, premature leaf dropping, reduced growth rates and increased susceptibility to other agents. Damage caused by ozone has been documented in many species, including white pine, red spruce, loblolly pine, black cherry, tulip poplar, short leaf pine and dogwood. Assessments of forest damage, both field studies and controlled chamber studies, strongly suggest that ozone inflicted damage to forest ecosystems is indeed real and is occurring at exposure levels significantly below the current U.S. ozone ambient standard of .12 ppm.

Ozone effects on agricultural crops has been conclusively demonstrated in both controlled laboratory and field investigations. In fact, the scientific information on the relationship between crop loss and ozone exposure is so extensive that actual dose-response curves have been developed for several important crop species. The U.S. EPA's National Crop Loss Assessment Network Study indicated that when crops are exposed to ozone levels of over .05 parts per million for seven hours a day during the growing season , losses of 10 percent or greater

in net yield will result in wheat, corn, soybeans and peanuts. Furthermore, ambient ozone in various parts of the United States may be responsible for the reduction in yield of up to 20 percent in soybeans, up to 33 percent in tomatoes, and up to 26 percent in beans . EPA estimates the potential cash crop losses due to ozone exposure to be as high as three billion dollars per year.

Ozone probably does not act alone to cause adverse health effects and terrestrial damage. The chemical and physical characteristics of the ambient atmosphere are extremely complex. Changing temperatures, ultra-violet light, natural turbulence and the continuous release of chemicals from both anthroporganic and natural sources into the air result in constant chemical transformation. Oxidants are continuously reacting with other chemical species in the ambient air. In some instances, oxidants join with other air pollutants to inflict synergistic damage to the human respiratory system and to terrestrial ecosystems. Oxidants also play a central role in promoting the formation of acidic air pollutants, both wet and dry.

Air quality managers and public health officials often view the sources of an air pollution effect in a very simplistic manner. This approach may be justified for extremely stable air pollutants, but is certainly not acceptable in dealing with oxidants. In addition to affecting public health and terrestrial ecosystem, oxidants promote or contribute to the following harmful effects:

1. The accelerated deterioration of building materials, historic monuments, and cultural resources.
2. Indirect health effects such as toxic metals leaching from soils and pipes exposed to acidified water
3. Regional visibility impairment
4. Acidified lakes, streams, and soils

Obviously, atmospheric scientists, environmental health scientists, and air quality regulators together face a significant challenge in attempting to reduce the ambient ozone/ oxidant levels in

both urban and rural areas. This challenge is complicated by the lack of a complete understanding of ozone/ oxidant formation and by the fact that ozone/ oxidants are transported up to hundreds of kilometers during which time they react with other pollutants. The presentations on the effects of ozone/ oxidants at this symposium have clearly illustrated that the current levels of exposure to ozone and oxidants cause extensive damage to humans, forests, crops and soils. We must take immediate action to reduce ozone/ oxidant presursor emissions . I urge the federal Canadian and United States environmental agencies to join with the state and provincial environmental agencies in each country to work cooperatively and aggressively to reduce excessive ambient concentrations of ozone/ oxidant which are inflicting damage in both countries.

# FORMATION DES OXYDANTS/OXIDANT FORMATION

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# OXIDANT FORMATION

## Conclusions and Recommendations:

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## Summary and Discussion

Within the Oxidant Formation session of this conference six speakers presented papers on various aspects of oxidant formation in the atmosphere. These can be roughly categorized in terms of three areas. Fred Lurman discussed chemical mechanism development and proposed various approaches for evaluating mechanisms which are currently in use or under consideration for application in models, or precursor emission/ozone relationships in urban areas. Marcia Dodge discussed the application of ozone/precursor emission relationships in the development of control strategy options within urban areas, while John Holmes discussed the California experience with regard to the air quality management of ozone as well as other oxidant species in the South Coastal basin. Two other talks presented in the session were associated with aspects of the chemical characterization of the transition region. This is the region associated with second and third day chemical transformations that occur outside the influence of the first day's transport of the urban plume, but as yet have not totally blended into the rural background. Jennifer Logan discussed ozone measurements in continental air and the implication of their temporal trends. While Greg Kok discussed the measurement and the implications of ozone as well as other oxidants, in particular, hydrogen peroxide in the boundary layer and free troposphere. Michael Trainer closed the session with a discussion on the measurement of hydrocarbons and oxides of nitrogen and the implications of these chemical constituents in ozone production processes in rural environments.

I would like, as part of my discussion of the session, to highlight some of the issues and outstanding problems resulting from gaps in our understanding of the oxidant formation process in the urban environment. This will be followed by a discussion of the regulatory implications of such knowledge gaps or uncertainties and I will conclude with some recommendations as to how one might proceed to resolve these outstanding issues.

The development of chemical mechanisms describing the photooxidation of hydrocarbon and nitrogen oxide constituents emitted into the atmosphere has drawn extensively from thermochemical kinetic principles which have provided theoretical estimates of reaction rate processes, as well as empirical results from laboratory kinetic studies of elementary reactions. The detailed reaction mechanisms hypothesized are compared against smog chamber experiments which consider various components and concentration levels of hydrocarbons and $NO_x$.

Such studies have been instrumental in the evolution of our understanding of the complex chemical processes associated with the production of ozone and other photochemical oxidants in the atmosphere. Mechanisms development has occurred by using data from smog chamber experiments as a basis set for truth, that is, mechanisms performance and validity has been measured and judged based upon the mechanisms ability to fit the concentration - time profiles of the experimental data. The assumption being that the smog chamber experiments provided a representative analogue of the chemical systems operative in real world polluted atmospheres, therefore allowing the extrapolation of the developed mechanisms to simulating the chemical transformations in polluted atmospheres.

As part of this development effort has evolved a rather loose methodology for characterizing the validity of chemical mechanisms. As mechanism testing and evaluation procedures identified limitations in the data bases and chamber systems, scientists began to question the degree of effort one should make to fit individual runs, series of runs, and runs between different experimental smog chamber systems.

We have seen that mechanism comparisons with chamber data can be very good. As a matter of fact, examples have been shown where one could not distinguish the observations from the predictions. This unfortunately provides an overly optimistic impression of the precision and accuracy of both the mechanism as well as the smog chamber. Underlying these fits are specified, but not always well characterized chamber parameters. These include the effects of chamber walls as sources and sinks for important chemical constituents participating in the photooxidation process. The limited quantitative characterization of wall sources and sinks introduces "chamber noise", which ultimately governs the limits of precision and accuracy of the mechanism. More importantly an unknown or incorrect specification of wall sources and sinks causes the mechanism to under or overpredict when applied in real world atmospheres. These limitations which cannot all be explicitly characterized, introduce contamination in the mechanisms, which can take the form of inherent noise or a systematic bias.

It has also been pointed out that much of our knowledge of chemical mechanisms has been gleaned from the empirical chamber data base, which has had to consider concentration regimes that are generally higher than that found in ambient urban air environments and definitely higher than levels in the transition and rural regions. Therefore, we have had to hypothesize that our theoretical understanding of the chemistry in the higher concentration regimes can be extrapolated down to the lower concentration levels. The lack of direct empirical evidence from chamber studies or any other source to verify the photooxidation processes at low concentrations of oxidant precursors is an issue of major contention.

Michael Trainer discussed one example of a study, which attempts to utilize atmospheric observations to diagnose the critical chemical constituents contributing to oxidant production in a rural environment. Such studies utilizing advanced instrumentation must be pursued as an alternative to smog chamber experimentation if we are to collect data to verify chemical transformation processes in the transitional and rural environments. In doing so we must also recognize the complexities that the dynamics of the atmosphere introduce making diagnostic interpretations of mechanisms quite difficult. But even with these caveats it would seem that progress in instrumentation technology and the importance of studying real world chemical systems suggests that atmospheric observations of increasing sophistication become a major component in the development of new generation chemical mechanisms.

In discussing mechanism uncertainties it should also be highlighted that our understanding of the details of the aromatic chemistry remains weak. If you recall from previous discussion in a companion session on measurements in the urban atmospheres, Lonneman indicated that aromatics can represent as much as 30% of the hydrocarbon burden in the atmosphere. Aromatics are a significant source of ozone production as a result of their participation in photooxidation processes.

Aromatic studies in smog chambers have not been successful in identifying many of the products of their decomposition. Most studies have only been able to identify 50 to 60% of the reacted carbon as product. This results in considerable speculation in describing the details of the aromatic mechanism in order to provide for acceptable time series for the conversion of NO to $NO_2$, and the production of ozone and other photochemical oxidants.

One might argue that if we reproduce the curves for NO, $NO_2$ and ozone, then we are probably doing a reasonable job in describing the aromatic oxidation chemistry overall. But the questions arise, are these products not observed or are they being removed from the system due to chamber artifacts. In either case the answers have important implications as to the mechanisms ability to predict the relationship between precursor hydrocarbon-$NO_x$ concentrations and ozone.

The secondary product chemistry of a variety of chemical reactions associating not only with the aromatics but even with some of the alkanes is not very well understood, and not treated in detail in many mechanisms. The problems introduced by uncertainties in alkane chemistry are probably less relevant to the urban oxidant production process, , but have major implications in the transitional, as well as these rural regions.

All of the issues discussed above have significant implications regarding the application of chemical mechanisms in the development and implementation of an ozone control strategy. The mechanisms which have demonstrated acceptable performance scientifically, based on comparison with smog chamber data with their implied precision and accuracy limitations, may not provide acceptable results for application by the regulatory community. By this I mean that the regulatory application may require better precision and accuracy performance from the mechanism in order for it to be an effective tool for developing quantitative control strategies. It has been observed that different mechanisms give different requirements for control in the atmosphere.

At issue is the precision and accuracy of these quantitative relationship, methods for their evaluation, and standards of acceptability (or success). Chamber noise discussed in the previous section has important implications on the limits of precision and accuracy of the quantitative relationship desired in regulatory applications. If the chamber effects are unknown or incorrectly specified, the result is a chemical mechanism that has most likely over- or under- compensated the radical production processes in order to achieve an acceptable fit of the chamber data. The application of such a mechanism in a regulatory model will result in a systematic bias in the quantitative relationship between precursor emissions and ozone production.

For example, the scientific community in reviewing the various sources of error associated with the chemical mechanism development process anticipates uncertainties of the order of plus or minus 30% in the mechanisms predictive capability when compared with chamber data. Establishing that this is a reasonable error limit when the mechanism is applied under real atmospheric conditions remains a critical issue which must be demonstrated if these approaches are to have any scientific

credibility. But more importantly if the 30% uncertainty is reflected in the control requirement of precursors (e.g., non methane hydrocarbons) to meet the ozone standard in a given city, the associated cost differentials can be both economically and socially prohibitive.

The recognition of this uncertainty and factoring it into the quantitative procedures required in state implementation plans to demonstrate a course of action for attaining the national ambient air quality standard for ozone would seem a logical first step to be taken by the regulatory community. The next step should be to establish realistic precision and accuracy performance standards for mechanisms to be used in quantitative models for control strategy development.

Based on the discussions above, our understanding of the chemistry occurring between urban, transitional, and rural regions must be further tested and developed and the mechanisms that result applied in regional models to be evaluated with real world observations.

Until such verified modeling approaches are developed the debate will continue as to whether regional ozone is primarily the result of 1) diluted urban pollution, 2) increased sources of oxides of nitrogen outside urban regions, 3) biogenic emissions and/or residual volatile organic compounds outside of urban regions, and 4) a combination of the above.

These are all relevant issues related to the resolution of regional air quality problems as are the questions raised by those individual cities which are along the prevailing flow downwind of other major metropolitan areas. These cities are concerned about the levels of ozone and ozone precursor reductions they might expect along their upwind border, since these will have significant impacts on the nature and extent of their ozone control strategy program.

Finally, there has been substantial progress made in the evaluation of models on the urban scale. As discussed at this meeting, urban photochemical oxidant models perform reasonably well providing comparison with observation of the order of plus or minus 50% and generally better for the more important hourly maximum periods. It is important to recognize that model evaluations performed to date, test the model's ability to simulate days in a deterministic sense. The models have not been tested to determine their ability to respond accurately to an emission perturbations, as we have no observational data sets to allow such needed performance evaluations.

An important aspect of data void is the lack of systematic trend data in cities of nonmethane hydrocarbon concentration, the essential component of our national control strategy program. It would seem imperative that systematic measurement of hydrocarbons be made to establish their long term trends so that we can verify the effectiveness of national and state emission control programs. This will also help in verifying the overall quality of hydrocarbon emission inventories which is being continually debated.

**Recommendations:**

Within the framework of this discussion I would like to propose the following recommendations:

1. In the development of chemical mechanisms for atmospheric simulation, procedures be established to map mechanisms identifying their critical nodes for radical initiation, propagation, and termination. This will allow the community to better understand subtle differences between mechanisms and interpretations of their application.

2. Chemical kinetic laboratory experiments should be performed to reconcile the differences in critical nodes between mechanisms which result from lack of knowledge of the chemical details of a reaction process (e.g., elementary reaction steps, fragmentation channels and yields).

3. Guidelines and standards for smog chamber operations and basic requirements for chamber characterization should be developed. The chamber performance characteristics must be documented and submitted to peer review, preferable through publication in the open literature. In addition a program of smog chamber intercomparison studies to determine internal bias among systems, variations in artifact effects and overall reproducibility of results between systems should be implemented.

4. An aggressive program in atmospheric field observation should be mounted to systematically build an atmospheric chemical observational data base for the purpose of diagnostic interpretation and evaluation of mechanisms.

5. A monitoring program for hydrocarbons in both urban and regional environments should be initiated with the intent to study long term trends in hydrocarbons and the success of control programs.

6. Regional models continue to be developed, intercompared and evaluated with all appropriate available data sets.

7. Observational networks be deployed with the specific purpose to test and evaluate regional air quality/deposition models.

# OXIDANT TRANSPORT AND MODELING

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During the course of this symposium there was a session on transport and modelling. The session covered a very wide geographical extent with results presented of an application of models in Japan, to North America, to eastern U.S. and to New York City. The extents of the modelling domains, about which results were reported, ranged from 3000 kilometers to roughly 300 kilometers on a side and corresponding order of magnitude difference in the horizontal grid lengths that scientists used.

What I would like to do is to try to point out certain ideas that came to me as someone who knows something about modelling atmospheric flow but is not an expert in atmospheric chemistry. I think the common thread one can see throughout the presentations is that model complexity is determined by available computer resources, as much as by science. There are always trade-offs made between the horizontal and vertical extents of which the models will consider, as well as the resolution and complexity of physical processess.

These trade-offs are determined by the resources available and the particular interest that one may have in trying to examine some particular aspect of the problem. Finally, the factor that Dr. Chang mentioned, a very real one, that is human patience. Nobody will or should undertake a modelling activity which is so complex that experiments can only be done once every 2 months. The demands made upon computer resources in order to tackle these problems are such that inevitably one limits the area and that immediately involves a question of boundary conditions and as well a question of initial conditions.

The other common thread that ran through the modelling session was the question of emissions. I suppose the one of the basic laws of modelling is "garbage in - garbage out". The emissions in fact, may represent garbage in a real sense, but if you have large uncertainties in the emission estimate, then of course the results you get out of the model, will have equally large uncertainties. Actually, the results will have more uncertainty because there is uncertainty in the model representation of the processing of the emission material.

What I would like to do now is summarize my thoughts in the modelling area as to what the problems are and where we seem to be making progress. First of all, I was quite impressed with the verifications such as they were, both from the point of view of the urban airshed model, the regional oxidants model of EPA. In fact, any model that can indicate where emissions data may be faulty, and in fact find out that to be true cannot be all wrong! However, the big problem in this area is essentially the number of realisations that can be performed. There is a big difference between this type of effort and another major modelling application, namely numerical weather prediction. That is that you carry out a weather prediction with your model with essentially new circumstances every day. Then you find out how the model performed. That way you can correct errors, discover what is wrong with the parameterization of physical processes in the model, test other assumptions that you have made and improve your understanding of what is going on. In the case of oxidants or other air pollution question, these data sets are extremely difficult and costly to obtain, and not at all the same as the sort of data sets which are routinely available for numerical weather prediction modelling.

The same thing goes with modelling verification. That is, having data on those critical aspects of the model output or intermediate variables that exist in order to gain confidence that you are describing the physics and chemistry correctly. It is very important to realize that a model which has very complex chemistry includes many many species. If you are going to use this model, you must put in a number for the concentration for each species. If someone says "Well, I don't know what it is", it is not good enough. If you do not put in a number the computer will send back a message "variable undefined". A modeler must put in a number and if no one has any number to give a modeler then he will make one up - he has to.

One of the things that concern me, as somewhat of a layman in the whole business of pollution modelling, is this business of uncertainty in emissions. What does one really have in terms of a model output with complex chemistry, if you have really very poor knowledge of the emissions? What does it mean when you use annual average emissions and you try to apply the model on an episodic basis?

I would like to re-emphasize a point made by Dr. Chang because I believe it is important. He talked about what he called, a "nested" strategy. Obviously, everybody would say "Well, if we have problems with boundary conditions why don't we just run the models on a global basis, then there are no horizontal boundary conditions. That of course, begs the question since if you ran it on a global scale you would still have to put in all those numbers, and if you do not know those numbers, then what is the point. As such, the nested strategy seems to me to make a lot of sense. As Dr. Demerjian said that the oxidant problem probably has at least three, if not more, regimes, in which one is interested in knowing what is going on.

Each of these regimes may have different chemical procesess which are dominant. So that one may want to look at a much finer scale and more detail in certain regions rather than others and yet one definitely has to worry about what is coming in from outside that region. That is why the nested strategy, whereby you start off by doing a simulation with a relatively coarse grid and you focus in to smaller areas makes sense. In that focusing, one may change the physics or chemistry you are applying in that particular area, if it is more appropriate on that scale. In many cases, certainly those cases that we are discussing here (episodic events of very high ozone levels) there is a role for a model specialization where one does not consider all of the physical processes. There should always be some quality control provided through a nesting strategy. If this nesting strategy is done with a model which is sufficiently capable to include a specialized physical or chemical model as one of its subsets, then it can be used as a guide for the proper interpretation of these specialized models.

A final point on the model verification is that we have a fundamental problem with respect to pollution modelling in my view and that is the mismatch between the scales of deposition, the scales of emission, and in fact what we are capable of measuring and modelling at this particular time. Whenever you have this particular type of mismatch, you have a great problem interpreting what the model is telling you as compared to a point measurement, because the results of the model inevitably are going to be some sort of average over space and time. Equally well from the physical point of view, you have the problem of physical processes taking place on much smaller space scales that you can possibly afford to model. So that model verification will be a very important problem. How do you interpret what the model output is telling you in the light of the verifying observations which are on a totally different scale?

The bottom line, in my view, is that modelling is making considerable progress, and that the major limitations to further progress is the need for observations to verify the models and greater attention to determination of emissions.

# MEASUREMENTS OF OZONE AND RELATED SPECIES

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# MEASUREMENTS OF OZONE AND RELATED SPECIES

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Measurements of ozone and its precursors in the troposphere are essential for understanding the complex chemical and meteorological processes involved in oxidant production. Measurements are also needed to evaluate models on which control strategies are based. This symposium has presented an impressive amount of new data but, at the same time, has revealed that much more is still needed although Pinkerton reminds us of the perennial problem of finding sufficient time and support to analyse data already on hand.

The papers by Kurtz and by Schemenauer discuss episodic events of high $O_3$ concentrations in southwestern Ontario and in rural Quebec, respectively. In the first session of the symposium Bates discusses in considerable detail the effects of episodic events on human health while Bernier and Skelly consider their implications on tree damage. Effects on agricultural crops is discussed briefly by Kurtz and is well documented elsewhere.

Kurtz points out that all of southwestern Ontario exceeds national standards for ozone concentrations on a regular basis in the warm season, with maximum values occurring in June and July. The fact that these maximum values are similar to those found in Germany should be matter of some concern since many view central Canada as being considerably "cleaner" than central Europe.

Both the frequency and duration of episodes in Ontario and Quebec and the concentration maxima decrease from south to north. The episodes are usually associated with the rear of slowly moving high

pressure regions and, consequently, with the influx of warm air from the south. Much of the ozone and the precursors associated with these episodes therefore originate south of the Canadian border. This conclusion is supported by the observations of Pinkerton in the forested regions in eastern U.S.A. which show a strong south to north gradient.

Although the importance of episodes to human health appears to be well established Pinkerton points out that there are uncertainties in the importance of the frequency and the duration of high concentrations on forests. Another uncertainty is how the effects of elevated concentrations depend on the stage of growth within the season.

Measurements to determine trends in ozone concentrations are important for a number of reasons: (1) the negative effect of ozone on photosynthesis has been demonstrated so that an upward trend in ozone levels may have serious consequences on bioproduction rates; (2) as a strong absorber of infrared radiation ozone plays a significant role in the "greenhouse effect", and (3) a comparison between observed and predicted trends provides an important test for the models.

Hunt shows that there has been a downward trend in ozone in the U.S.A., amounting to 10% between 1979 to 1985. The data was obtained from the National Air Monitoring stations which are located in areas of high populations and, consequently, of high levels of pollution. Kurtz finds very little evidence for an ozone trend in southwestern Ontario with the exception of a slightly higher annual average in 1983 which is suspected of being caused by atypical meteorological conditions in that year. These measurements were also taken in relatively populated sites which were also receiving much of their transport from the U.S.A. Pinkerton finds considerable variability in the yearly averages in the forestry regions and stresses the need for long term data bases.

These observations are somewhat in variance with the study on Global Stratospheric Chemistry (1986) which reports that tropospheric ozone concentration has increased in the northern hemisphere by several

percent over the past decade due to human activity. The discrepency may, in part, be due to the difference in spatial scales being considered - a recurrent theme in this symposium. The hydrocarbon to $NO_x$ ratios can be very different in highly polluted urban centres, in rural areas or when averaged over an entire hemisphere. Long range transport obviously plays an important part as evidenced by the regional similarities in ozone concentration patterns noted by Schemenauer and by Logan.

Hunt's analysis of the National Air Monitoring network shows that volatile organics have decreased by 12% in the urban centres while there has been only a slight decrease in $NO_x$ which would favour a decrease in ozone. Very little data is available on the ratio of these precursors on rural and hemispheric scales.

Because of the large differences in reactivity of different hydrocarbons and in their relative roles in producing $HO_x$ radicals, determination of the speciation of the hydrocarbons in each of the areas are of paramount importance. Lonneman presents a a detailed analysis of the composition of volatile organic (VOC) in a number of urban sites from 1984 to 1986. He addresses the difficult task of trying to differentiate VOC emissions from automobile and industrial sources. He uses acetylene as a tracer for tail-pipe emissions from automobiles and concludes that automobiles are largely responsible for olefin emissions while paraffins are emitted mainly from non-vehicle sources. One difficulty in this analysis is that, in addition to tail pipe emissions, vehicles contribute to VOC emissions through fuel storage and carburetors which might have quite different compositions. However, the analysis does reveal a number of important findings such as the fact that paraffins are the most abundant class of hydrocarbons in urban areas. On the other hand, in the non-urban areas, natural emissions of VOC's such as terpenes may dominate natural sources and must be measured and characterized.

Another reason for local and regional scale differences is transport. Most of the measurements have been made near the surface in the planetary boundary layer which is characterized by relatively rapid, vertical mixing. Much greater horizontal transport occurs in the overlying free troposphere region. These two regions are frequently isolated, particularly during nighttime inversions and differences in the dominant chemical processes occur. For example, both Galvin and Schemenauer finds much higher ozone concentrations at mountain sites compared to valleys where, presumably, ozone is destroyed more effectively by the higher concentrations by NO. Measurements of vertical gradients of relevant species is of very important.

Although mountain measurements are useful for a number of reasons they are not ideal for determining vertical gradients. They are not entirely free of boundary layer effects and of course, not being highly mobile, give limited geographical coverage. Aircraft measurements provide much better spatial distributions but are too expensive to attain the desired temporal data base. An attractive alternative is the use of either tethered or free-floating balloons. Relatively inexpensive ozonesondes are available and other lightweight instruments capable of measuring other species are now becoming available. The use of balloon measurements is a major component in the Tropospheric Ozone Research (TOR) program about to be launched in Europe.

In addition to measurements of ozone and its precursors there is a need to measure the intermediates and end products of photooxidation. The primary reason is that such measurements provide very sensitive tests for model evaluation. Some of the intermediates, such as hydrogen peroxide and formaldehyde are important sources of free radicals. Hydrogen peroxide, itself a strong oxidizer, is believed to be particularly important in the conversion of $SO_x$ to sulfuric acid. Many of the oxygen and nitrogen containing intermediates such as aldehydes, PAN and nitrosamines are harmful to human health. The

dependence of the production of these noxious compounds on the VOC/NOx ratio should be considered in planning oxidant control strategies.

PAN is a particularly interesting compound and its measurement is becoming very fashionable. Long known to be a powerful lacrymator and phytotoxic agent, PAN is now being found to be a major mutagen. It also has important chemical properties. The thermal decomposition of PAN is very strongly temperature dependent, resulting in an atmospheric lifetime ranging from 2 hrs at 300 K to 200 days at 260 K. Thus, for example, PAN formed in an urban site and convected into the upper free troposphere can be transported over very large distances. If it then subsides to lower levels where the temperature is higher it decomposes to yield $NO_2$ which will initiate photooxidation at the new location.

Producing a "wish list" of what substances to measure and where is relatively easy. Much more difficult is finding suitable techniques to make these measurements. For example, the hydroxyl radical is by far the most important oxidant in the atmosphere. But its very reactivity makes its ambient concentration so low that its measurement has remained virtually unattainable. On the other hand the relatively straightforward technique of gas chromatography can be used to differentiate the VOCs but is so cumbersome and tedious that little of this important information is available.

Another problem is the cost associated with the number of network sites required for model evaluation. This has limited the techniques used for measurements at these sites to relatively unspecific and, at times, questionable methods such as filter techniques for gaseous species. There is an important need for quality control and assurance of the data obtained from these networks. There is also a need to develop relatively inexpensive alternatives such as instruments based on chemiluminescence or fluorescence. Such instruments are becoming available but, in turn, need to be referenced to more specific, but relatively more expensive, spectroscopic methods. It is gratifying to

see that "double blind" comparison studies are now being made to characterize instrument performance.

Having outlined why, what and where species related to oxidants should be measured I would like to conclude with two "caveats". First, I think we should be very careful about drawing premature conclusion on the basis of a limited measurement set. We need to be very careful in having good data on oxidants, their precursors and their sinks on a range of spatial scales - urban, regional and even hemispherical - before deciding on the most effective abatement strategy . Finally, I think that pressure to provide answers to these very complex problems by an unrealistic deadline must be resisted. Measurements are essential; but incomplete or bad measurements are probably worse than no measurements at all. They are a waste of scarce resources and can lead to totally misleading conclusions.

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ANNEXES/APPENDICES

# ANNEXE I/APPENDICE I

## PROGRAMME/PROGRAM

ANNEXE I

SYMPOSIUM NORD-AMÉRICAIN SUR LES OXYDANTS

PROGRAMME

MARDI, 24 FÉVRIER 1987

16 h 00 à 18 h 30 — Inscription des participants, Étage des Congrès

18 h 30 à 20 h 00 — Réception (bar aux frais des participants) Salon Borduas

MERCREDI, 25 FÉVRIER 1987

08 h 00 — Inscription des participants, Étage des Congrès

09 h 15 — Mots de bienvenue
*Jean-Claude Deschênes, sous-ministre*
*Ministère de l'Environnement du Québec*

SALON SUZOR CÔTÉ — PREMIÈRE SÉANCE - LES OXYDANTS ET LEURS EFFETS SUR LA SANTÉ HUMAINE ET LES ÉCOSYSTÈMES TERRESTRES
Président: *Dr Tom Brydges*
*Service de l'Environnement atmosphérique*
*Environnement Canada*

09 h 30 — Le dépérissement de la forêt feuillue du sud-est du Québec: la pollution atmosphérique est-elle impliquée?
*Dr Bernard Bernier*
*Département des sciences forestières*
*Université Laval*

10 h 00 — Les effets induits par les oxydants sur les écosystèmes forestiers: les dommages cachés versus le dépérissement dévastateur de la forêt, la réalité versus la conjecture
*Dr John M. Skelly*
*Département de pathologie végétale*
*Université de l'état de Pennsylvanie*

10 h 45 — Pause

11 h 00 — Les effets de l'ozone sur les individus et la population humaine
*Dr David Bates*
*Département de médecine*
*Université de Colombie-Britanique*

12 h 00 — Déjeuner

SALON SUZOR CÔTÉ — DEUXIÈME SÉANCE - FORMATION DES OXYDANTS
Président: *Dr Jan Bottenheim*
*Service de l'environnement atmosphérique*
*Environnement Canada*

13 h 30 — La chimie de la formation des oxydants: son rôle dans le développement de stratégies de contrôle efficaces
*Dr Marcia C. Dodge*
*Laboratoire de recherche sur les sciences atmosphériques*
*Agence américaine de protection de l'environnement*

14 h 00 — Approches dans le développement des mécanismes des oxydants photochimiques
*Dr Alan Lloyd*
*Recherche et technologie environnementales*
*Californie*

14 h 30 — La production d'ozone dans les milieux ruraux
*Dr Jennifer Logan*
*Département des sciences de la terre et des planètes*
*Université Harvard*

15 h 00 — Pause

15 h 15 — Les considérations de la chimie dans la stratégie de contrôle de l'ozone en Californie
*Dr John R. Holmes*
*Direction de la recherche*
*Commission des ressources atmosphériques de la Californie*

15 h 45 — Les oxydants atmosphériques du soufre(IV)
*Dr Gregory L. Kok*
*Centre national de la recherche atmosphérique (États-Unis)*

16 h 15 — Les effets des sources naturelles d'hydrocarbures sur l'ozone en milieu rural: modélisation et observations
*Dr Michael Trainer*
*Laboratoire d'aéronomie*
*Administration nationale de l'atmosphère et de l'océan (États-Unis)*

16 h 45 — Ajournement

JEUDI, 26 FÉVRIER 1987

SALON SUZOR CÔTÉ — TROISIÈME SÉANCE - TRANSPORT ET MODÉLISATION DES OXYDANTS
Président: *Dr Alan M. Dunker*
*Département des sciences de l'environnement*
*Laboratoire de recherche de General Motors (États-Unis)*

09 h 00 — Le développement et les applications du modèle régional sur les oxydants
*Dr Robert G. Lamb*
*Laboratoire de recherche des sciences atmosphériques*
*Agence américaine de protection de l'environnement*

09 h 30 — La formation et le transport des oxydants analysés à l'aide du modèle STEM
*Dr Gregory Carmichael*
*Département de génie chimique et de génie des matériaux*
*Université d'Iowa*

10 h 00 — Application d'un modèle de bassin atmosphérique urbain à la région métropolitaine de New York
*Dr S. Trivikrama Rao*
*Direction des ressources atmosphériques*
*Ministère de la Conservation de l'environnement de l'état de New York*

10 h 30 — Pause

10 h 45 — Une étude théorique de la distribution régionale des oxydants en Amérique du Nord
*Dr Julius S. Chang*
*Centre national de la recherche atmosphérique (États-Unis)*

11 h 15 — Formation et transport des oxydants associés aux émissions d'un complexe pétrochimique en Ontario
*Dr Mario Lusis*
*Direction des ressources atmosphériques*
*Ministère de l'Environnement de l'Ontario*

12 h 00 — Déjeuner

SALON SUZOR CÔTÉ — QUATRIÈME SÉANCE - SURVEILLANCE DES OXYDANTS
Président: *Jean A. Roy*
*Direction générale du milieu atmosphérique*
*Ministère de l'Environnement du Québec*

13 h 30 — Analyse des précurseurs des oxydants et liens avec la formation de l'ozone
*William A. Lonneman*
*Laboratoire de recherche sur les sciences atmosphériques*
*Agence américaine de protection de l'Environnement*

14 h 00 — Un examen des niveaux d'ozone dans des zones forestières choisies de l'Est des États-Unis
*Dr John E. Pinkerton*
*Conseil national de l'industrie du papier pour l'assainissement de l'atmosphère et des cours d'eau (États-Unis)*

14 h 30 — Tendances nationales et régionales des mesures de dioxyde d'azote et de l'ozone dans l'air ambiant: 1975-1984
*William F. Hunt*
*Bureau de la planification et de la normalisation de la qualité de l'air*
*Agence américaine de protection de l'environnement*

15 h 00 — Pause

15 h 15 — Une revue des problèmes des oxydants en Ontario
*Joël Kurtz*
*Direction des ressources atmosphériques*
*Ministère de l'Environnement de l'Ontario*

15 h 45 — Mesure de l'ozone et d'autres oxydants en milieu montagneux dans l'Est de l'Amérique du Nord
*Philip J. Galvin*
*Ministère de la Conservation de l'environnement de l'état de New York*

16 h 15 — Les variations géographiques des concentrations de l'ozone au Québec à des sites de faible et haute altitude en milieu rural
*Dr Robert S. Schemenauer*
*Service de l'environnement atmosphérique*
*Environnement Canada*

16 h 45 — Ajournement

19 h 30 — Dîner officiel offert par le ministre de l'Environnement du Québec
*M. Clifford Lincoln*
Hôtel le Château Frontenac, Salon Frontenac

VENDREDI, 27 FÉVRIER 1987

SALON SUZOR CÔTÉ — CINQUIÈME SÉANCE - CONCLUSIONS ET RECOMMANDATIONS
Séance plénière portant sur les résultats du symposium
Modérateur: *Jean Piette*
*Direction des relations intergouvernementales*
*Ministère de l'Environnement du Québec*

09 h 00 — Effets sur la santé humaine et les écosystèmes terrestres
*Michael Bradley*
*Directeur exécutif*
*Bureau de coordination de la gestion de l'air dans des états du Nord-Est*

Formation des oxydants
*Dr. Kenneth Demerjian*
*Centre de recherche de l'atmosphère*
*Université de l'état de New York à Albany*

Transport et modélisation des oxydants
*Dr. Philip E. Morrilees*
*Service de l'environnement atmosphérique*
*Environnement Canada*

Surveillance des oxydants
*Dr Harold I. Schiff*
*Université de York (Toronto)*

12 h 00 — Ajournement

APPENDIX

# NORTH AMERICAN OXIDANT SYMPOSIUM

## PROGRAM

**TUESDAY, FEBRUARY 24, 1987**

4:00 to 6:30 p.m. Registration, Convention Floor 3rd Floor

6:30 to 8:00 p.m. Cash bar reception, Salon Borduas 3rd Floor

**WEDNESDAY, FEBRUARY 25, 1987**

8:00 a.m. Registration, Convention Floor 3rd Floor

9:15 a.m. Official Opening
*Jean-Claude Deschênes*
*Deputy Minister*
*Québec Ministry of Environment*

SALON SUZOR CÔTÉ **SESSION I - OXIDANTS AND EFFECTS ON HUMAN HEALTH AND TERRESTRIAL ECOSYSTEMS**
Chairman: *Dr. Tom Brydges*
*Atmospheric Environment Service*
*Environment Canada*

9.30 a.m. Decline of the Deciduous Forest in Southeastern Québec: Is Air Pollution Involved
*Dr. Bernard Bernier*
*Department of Forestry Sciences*
*Laval University*

10:00 a.m. Oxidant Induced Effects to Forest Ecosystems: Hidden Injury vs Devastating Forest Declines; Reality versus Conjecture
*Dr John M. Skelly*
*Department of Plant Pathology*
*The Pennsylvania State University*

10:45 a.m. Break

11:00 a.m. The Effects of Ozone on Individuals and Human Populations
*Dr. David Bates*
*Department of Medicine*
*University of British Columbia*

12:00 a.m. Lunch

SALON SUZOR CÔTÉ **SESSION II - OXIDANT FORMATION**
Chairman: *Dr. Jan W. Bottenheim*
*Atmospheric Environment Service*
*Environment Canada*

1:30 p.m. Chemistry of Oxidant Formation: Implications for Designing Effective Control Strategies
*Dr. Marcia C. Dodge*
*Atmospheric Sciences Research Laboratory*
*U.S. Environmental Protection Agency*

2:00 p.m. Approaches to the Development of Photochemical Oxidant Mechanisms
*Dr Alan Lloyd*
*Environmental Research and Technology*
*California*

2:30 p.m. Ozone Production in Rural Areas
*Dr. Jennifer Logan*
*Department of Earth and Planetary Sciences*
*Harvard University*

3:00 p.m. Break

3:15 p.m. Chemical Considerations in California's Ozone Control Strategy
*Dr. John R. Holmes*
*Research Division*
*California Air Resources Board*

3:45 p.m. Atmospheric Oxidants for Sulfur (IV)
*Dr. Gregory L. Kok*
*National Center for Atmospheric Research*

4:14 p.m. Impacts of Natural Hydrocarbons in Rural Ozone: Modeling and Observations
*Dr. Michael Trainer*
*Aeronomy Laboratory*
*National Oceanic and Atmospheric Administration*

4:45 p.m. Adjournment

**THURSDAY, FEBRUARY 26, 1987**

SALON SUZOR CÔTÉ **SESSION III - OXIDANT TRANSPORT AND MODELING**
Chairman: *Dr. Alan M. Dunker*
*Environment Science Department*
*General Motors Research Laboratory*

9:00 a.m. Design and Applications of the Regional Oxidant Model
*Dr. Robert G. Lamb*
*Atmospheric Sciences Research Laboratory*
*U.S. Environmental Protection Agency*

9:30 a.m. Oxidant Transport and Formation Analyzed from STEM Model Applications
*Dr. Gregory Carmichael*
*Department of Chemical and Materials Engineering*
*University of Iowa*

10:00 a.m. Application of the Urban Airshed Model for the New York Metropolitan Area
*Dr. S. Trivikrama Rao*
*Division of Air Resources*
*New York State Department of Environmental Conservation*

10:30 a.m. Break

10:45 a.m. A theoretical Study of Regional Oxidant Distribution in North America
*Dr Julius S. Chang*
*National Center for Atmospheric Research*

11:15 a.m. Oxidant Formation and Transport from Petrochemical Complex Emissions in Ontario
*Dr Maris Lusis*
*Air Resources Branch*
*Ontario Ministry of the Environment*

12:00 a.m. Lunch

SALON SUZOR CÔTÉ **SESSION IV - OXIDANT MONITORING**
Chairman: *Jean A. Roy*
*Director-General of Atmospheric Environment*
*Ministère de l'Environnement du Québec*

1:30 p.m. The Measurement of Oxidant Precursors and their Relationship to Ozone Formation
*William A. Lonneman*
*Atmospheric Sciences Research Laboratory*
*U.S. Environmental Protection Agency*

2:00 p.m. An Examination of Ozone Levels in Selected Forested Areas of the Eastern United States
*Dr. John E. Pinkerton*
*National Council of the Paper Industry for Air and Stream Improvement*

2:30 p.m. National and Regional Trends in Ambient Ozone and Nitrogen Dioxide Measurements: 1975-1984
*William F. Hunt*
*Office of Air Quality Planning and Standards*
*U.S. Environmental Protection Agency*

3:00 p.m. Break

3:15 p.m. A Review of the Ontario Oxidant Problems
*Joel Kurtz*
*Air Resources Branch*
*Ontario Ministry of the Environment*

3:45 p.m. Measurement of Ozone and Other Oxidants at Mountain Sites in Eastern North America
*Philip J. Calvin*
*New York State Department of Environmental Conservation*

4:15 p.m. Geographic Variations of Ozone Concentrations at High and Low Elevation Rural Sites in Québec
*Dr. Robert S. Schemenauer*
*Atmospheric Environment Service*
*Environment Canada*

4:45 p.m. Adjournment

7:30 p.m. Official Dinner Hosted by Québec Environment Minister
*M. Clifford Lincoln*
Hôtel Le Château Frontenac, Salon Frontenac

**FRIDAY, FEBRUARY 27, 1987**

SALON SUZOR CÔTÉ **SESSION V - CONCLUSIONS AND RECOMMENDATIONS**
Plenary Session on the Symposium Findings
Moderator: *Jean Piette*
*Director of Intergovernmental Affairs*
*Ministère de l'Environnement du Québec*

9:00 a.m. Effects on Human Health and Terrestrial Ecosystems
*Michael Bradley*
*Executive Director*
*Northeast States for Coordinated Air Use Management*

Oxidant Formation
*Dr. Kenneth Demerjian*
*Atmospheric Research Center*
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Oxidant Transport and Modeling
*Dr. Philip E. Merilees*
*Atmospheric Environment Service*
*Environment Canada*

Oxidant Monitoring
*Dr. Harold I. Schiff*
*York University*

12:00 Adjournment

# ANNEXE 2/APPENDICE 2

## LISTE DES PARTICIPANTS/LIST OF PARTICIPANTS

# SYMPOSIUM NORD-AMÉRICAIN SUR LES OXYDANTS
# NORTH AMERICAN OXYDANT SYMPOSIUM

**Québec, les 25, 26 et 27 février 1987**

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ANNEXE 3/APPENDICE 3

# THE DECLINES OF THE DECIDUOUS FOREST IN SOUTHEASTERN QUÉBEC: IS AIR POLLUTION INVOLVED

# The Decline of the Deciduous Forest in Southeastern Québec: is Air Pollution Involved?

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## Abstract

The deciduous forest of southeastern Québec is dominated by sugar maple (Acer saccharum Marsh.). This species and some of its associated species are declining at an alarming rate at several rural locations since 1980. The study area, located south of the St.Lawrence River and mainly in the Appalachians between Québec City and the State of Maine, covers about 17 000 km². A study on the foliar nutrient status of a great number of maple stands in this region since 1983 revealed widespread deficiencies of phosphorus (P) and more noticeably potassium (K) in the declining sugar maple stands. The deficiencies are accompanied by visual symptoms[1] that are probably unique to the current decline situation. To our knowledge, they have not been reported in previous declines in the deciduous forest of northeastern North America. Nutrient deficiencies have developed in recent years and we believe they play a key role in the forest decline by constituting a decisive predisposing, or inciting, stress factor. The origins of these nutrient disturbances are discussed in the light of several hypotheses that examine the effects of air pollution on forests.

## Résumé

La forêt feuillue du sud-est du Québec est dominée par l'érable à sucre (Acer saccharum Marsh.). Cette essence et quelques essences compagnes dépérissent d'une façon alarmante dans plusieurs localités rurales depuis 1980. Le territoire étudié couvre quelque 17,000

*1 The illustration of foliar symptoms (not shown in this text) is emphasized in the presentation.*

km² au sud du St-Laurent, principalement dans les Appalaches, entre la ville de Québec et la frontière américaine du Maine. Un inventaire du statut nutritif conduit dans un grand nombre d'érablières de ce territoire depuis 1983 a révélé l'existence étendue de carences en phosphore (P) et surtout en potassium (K) dans les érablières en voie de dépérissement. Ces carences s'accompagnent de symptômes[2] qui sont vraisemblablement spécifiques à la situation actuelle du dépérissement, n'ayant pas, à notre connaissance, été rapportés dans des cas antérieurs de dépérissement de la forêt feuillue dans le nord-est américain. Elles se sont développées au cours des récentes années et on croit qu'elles jouent un rôle clé dans le dépérissement de la forêt. L'approvisionnement insuffisant en éléments nutritifs peut constituer un facteur de stress prédisposant décisif. L'origine de ces perturbations de nutrition est discutée à la lumière des diverses hypothèses émises sur les effets de la pollution atmosphérique sur la forêt.

## Introduction

Since the beginning of the present decade, the deciduous forest of southeastern Québec has been showing signs of an abnormal, progressive decline. Recent surveys show that sugar maple, the dominant species of this forest, is declining in much of its range in southern Québec (Bordeleau, 1986; Carrier, 1986).

Although variation exists in the level of forest decline, the decline phenomenon is intensifying and is of growing concern (Carrier, 1986; Robitaille, 1986).

The production of maple syrup is a tradition in Québec and the management of stands for this product has undergone few changes in recent decades except for the introduction of vacuum systems for sap collection in the early 1970's. Nevertheless, several producers have retained the traditional sap collection by buckets and taps. But the

*2. L'illustration des symptômes foliaires (non reproduits ici) occupe une place centrale dans cet exposé.*

method of sap collection, whether by traditional means or by vacuum, is not seen as a contributing factor to the maple decline (Carrier, 1986).

During the last ten years the forest has been subjected to various biotic and abiotic stresses. Severe defoliations by the forest tent caterpillar (Malacosoma disstria) took place in the early 1980's mostly in the southern part of the Appalachian Highlands (Lachance et al., 1984) and unusual drought conditions occurred in 1983. These natural stresses undoubtedly contributed to tree death in several maple stands; however the above stresses alone cannot explain the present decline phenomenon which has started in certain areas before the 1980's and which is progressing in sites that had totally escaped defoliations by insects.

## Symptoms associated with the decline

General symptoms. The general symptoms of decline of the deciduous forest in southeastern Québec are not significantly different from those which have been reported in previous declines and attributed to natural factors (Sinclair, 1964): shoot growth reduction resulting in a clustering of leaves; reduction of main stem radial growth resulting in slow closure of tapholes; reduction of leaf area imparting a more open crown; death of twigs and small branches that do not survive the winter, followed by the death of larger branches the following year; formation of adventicious shoots on the trunk and large limbs accompanying the crown decline; and invasion of large roots by *Armillaria*, a root pathogen normally held in check in vigorous trees. Other previously observed symptoms such as the deterioration of fine roots and the depletion of organic reserves are presumably applicable to the current decline situation because they are evidence of poor tree functioning and they accompany the other disturbances (Sinclair, 1964).

Even though these symptoms are easily observable in the declining forest of southeastern Québec, they are not specific to any particular cause and, therefore, cannot be used for identifying causal fac-

tors. However, in addition to these general symptoms, other symptoms are present which are believed to be unique to the present situation because, to our knowledge, they have not been reported in previous declines of the deciduous forest in northeastern North America.

Specific symptoms: a diagnostic tool. In discussing the forest decline phenomenon, Prinz (1985) emphasized that attempts to explain the causes of forest decline have to fulfill the following three conditions:

a) it must be possible to connect all the specific symptoms of the decline to the causal factor in question;

b) the temporal development of the decline must coincide with the development of the causal factor, including consideration of the cumulative effects;

c) the spatial distribution of the decline must largely coincide with the distribution of the causal factor.

In the case of the present decline of the deciduous forest in southeastern Québec, the fulfillment of these conditions has not yet been substantiated. However the foliar symptomatology specific to the declining forest is becoming more and more apparent. This aspect is essential because Prinz's first condition assumes an adequate knowledge of the specific decline symptoms. Furthermore, this knowledge provides a good part of the information necessary to fulfill the other two conditions proposed by Prinz (loc. cit.). For this reason, this presentation emphasizes illustrations of the most common foliar symptoms in declining maple stands. Some of these symptoms, such as dark green, "cupped" leaves, can serve as early warning signs of decline because they precede the first manifestation of shoot death. We believe that the typical symptoms of nutrient deficiency that follow are characteristic of the declining forest in the current situation in Québec. In the study region, these deficiency symptoms are principally those of K and/or P.

These deficiencies have only developed in recent years. Their development reveals a serious problem of nutrient imbalance suggesting that this stress probably plays a major role in the forest decline.

## Nutrient deficiencies and forest decline

Before discussing the possible causes of the observed nutrient disturbances, it is necessary to consider whether the observed nutrient deficiencies are a cause or a consequence of the decline. Three reasons cause us to reject the hypothesis that the symptoms are a consequence of the decline:

a) to our knowledge, these symptoms have never been reported in previous cases of decline of the deciduous forest in northeastern North America;

b) an important part of the deciduous forest of southeastern Québec was subjected to repeated insect defoliation over a period of two or three years; although these defoliations can affect nutrient cycling and even cause tree decline, the observed nutrient deficiency symptoms occur in sites independent of whether they have been defoliated by insects or not;

c) the nutrient imbalance of the forest can be corrected by appropriate fertilizer applications that eliminate nutrient deficiency symptoms (Bernier and Brazeau, in prep.).

An analysis based on a three year study of the foliar nutrient status in some 70 maple stands revealed that K deficiency is a widespread phenomenon, occurring more frequently than P deficiency (Bernier and Brazeau, in prep.). Nevertheless P deficiency is a striking feature in many declining maple stands of the St.Lawrence Lowlands and the Québec Appalachians. Associated with these deficiencies are early leaf senescence and the decline of tree crowns.

The present decline situation in Québec has both similarities and differences with the forest decline currently reported in Central Europe. For example, nutrient deficiencies have also been associated with the forest decline in Germany (Huettl, 1986; Rehfuess, 1980, 1983; Zöttl, 1985a, 1985b; Zöttl and Huettl, 1985) and most researchers attribute a major role to the nutritional disturbances in these cases of forest decline. Differences between the European decline and the Québec decline show up mainly in the nature of the observed deficiencies: Mg deficiencies are common in Germany whereas they have seldom been noticed in areas of the deciduous forest of southeastern Québec that we have studied. Besides, to our knowledge, P deficiencies have not been reported in declining forests in Central Europe.

Do the nutrient disturbances originate from air pollution?

If we recall the first condition set forth by Prinz (1985) to explain the causes of forest decline, it is possible to affirm the existence of symptoms that are probably specific to the decline situation in southeastern Québec. Although the nature of the deficiency symptoms is now known to a large extent, much remains to be understood as to which processes are involved in their development. It seems certain that we are facing major nutritional disturbances which probably relate to several of the hypotheses put forward regarding the role of air pollution on forests and which have been extensively reviewed (Evans, 1982; Kozlowski and Constantinidou, 1986; McLaughlin, 1985; Guderian et al., 1985; Morrison, 1984; Roberts, 1984). Some effects of air pollution seem to be: 1) cation leaching within the rooting zone, accentuated by an excess of non adsorbed anions of anthropogenic sources (Foster, 1985; Huettl, 1986; Johnson et al., 1985); 2) soil acidification induced by acidic deposition resulting in the solubilization of heavy metals that may be in concentrations toxic to fine roots (Ulrich, 1983) and which may also indirectly reduce P uptake; 3) a surplus of anthropogenic $NO_3^-$ creating an increased demand for other nutrients with a negative effect

on mycorhizal symbioses (McLaughlin, 1985) which plays a well-known role in tree nutrition, particularly for P acquisition; and 4) an increased foliar leaching under acidic deposition and photooxidant occurrence (Cronan, 1984; Guderian et al., 1985; Scherbatskoy and Klein, 1983; Skeffington and Roberts, 1985; Wood and Bormann, 1975; Zöttl, 1985a). This latter point may particularly apply to K in view of its relative abundance in the leaf apoplasmic solution as a free ion. According to Miller (1984) replacement mechanisms would be sufficiently rapid to resupply nutrients leached from plant leaves unless tissues are damaged by additional stresses such as ozone.

It seems appropriate to us to bring in here the following rectification: In a seminar on maple decline held last May in Québec City we indicated that foliar lesions caused by ozone were associated with nutrient deficiency symptoms (Bernier and Brazeau, 1986a; 1986b). Since that time we have revised our interpretation: foliar lesions presumably attributed to ozone are much less extensive than previously believed. Nevertheless, this does not eliminate the possibility of a subtile, asymtomatic action of oxidants as has been recently reported in Northeastern U.S.A. (Wang et al., 1986).

With repect to the two other conditions that must be fulfilled in order to explain the cause of forest decline (Prinz, 1985), we cannot speculate as to the coincidence in time and space of the decline with the causal factor, because the latter is only hypothetically known. What is known, however, is that wherever the forest is declining, the symptoms of nutrient deficiencies noted above are present. Therefore we have been led to assume that the spatial distribution of the decline probably coincides with the causal factor.

Southeastern Québec is one of the most severely polluted regions of Canada: the annual inputs of $SO_4^{2-}$ and $NO_3^-$ in wet deposition alone are in the order of 40-60 kg $ha^{-1}$ and 10-30 kg $ha^{-1}$, respectively (Rennie, 1986). The concentrations of ozone are largely unknown except

for the observations in the rural St.Lawrence Lowlands by Maltais and Archambault (1985) for one year: measured concentrations varied from 80-150 nL $L^{-1}$. Several soils of the study area are inherently poor in K, particularly in a geographical belt surrounding the Thetford Mines ophiolitic complex. The decline is most severe in that region (Bordeleau, 1986). However, K deficiencies are not limited to that area only but generally occur throughout the study region in which there are a great diversity of geological formations (St-Julien and Hubert, 1975) and soils (Baril, 1974). Similarly, P deficiencies are sporadically present throughout the study area (Bernier and Brazeau, in prep.).

A study of foliar nutrient levels and of soil nutrient pools revealed that foliar P was correlated to the pool of available P in the forest floor, whereas foliar K levels were correlated with exchangeable K in the surface mineral horizons (Bernier et al., 1985). These observations suggest that changes of soil chemistry in the rooting zone may result in a reduction of nutrient availability, a possibility which seems to be supported by the observations of Gagnon et al. (1986). Foliage deficient in P or K has reduced rates of translocation of these nutrients and abnormally low rates of K and P return in the litterfall (Bernier and Brazeau, in prep.). This results in lower and less efficient nutrient turnover in the cycling of nutrients within the ecosystem.

## Conclusion

The observations reported here suggest that nutrient deficiencies probably play a direct, major role in the forest decline, similar to several situations reported in Central Europe (Guderian et al., 1985; Zöttl and Huettl, 1985). This can be caused by reduced levels of available nutrients in the rooting zone or -- especially in the case of K -- by increased foliar leaching, or by other, as yet undefined, disturbances in nutrient cycling. Such changes are believed to result from anthropogenic stresses. The present situation urgently needs additional

research to precisely define the origin of the forest decline phenomenon.

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